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LOW-TEMPERATURE LUBRICATING ENGINE OIL ADDITIVES

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ARMOUR RESEARCH FOUNDATION
ILLINOIS INSTITUTE OF TECHNOLOGY

APRIL 1953

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LOW-TEMPERATURE LUBRICATING ENGINE OIL ADDITIVES

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Armour Research Foundation
Illinois Institute of Technology

April 1953

Materials Laboratory
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Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

FOREWORD

This is a final report presenting research conducted by the Armour Research Foundation of Illinois Institute of Technology on low temperature lubricating oil additives under the sponsorship of the Power Plant Laboratory, Directorate of Laboratories, and the Materials Laboratory, Directorate of Research, Wright Air Development Center. This project was conducted under Contract No. AF 33 (038)-1644 and was initiated under Research and Development Order No. 613-12, "Aircraft Fuels and Lubricating Oil". Research was initiated on 10 February 1949 under the administration of the Power Plant Laboratory, Directorate of Laboratories, and was transferred on 11 August 1951 to the directorship of the Materials Laboratory, Directorate of Research, Wright Air Development Center. Project engineer was Lt C. D. Mercer.

ABSTRACT

The work reported was carried out to evaluate the limits of utility of commercial pour point depressants and viscosity index improvers with mineral oils, to determine the essential structural features of a pour point depressant, and to extend present knowledge of the mechanism of pour point depression.

The thixotropy exhibited by Pennsylvania 150 Neutral oil below its pour point, studied with rotational concentric cylinder viscometers, was resolved into two processes occurring simultaneously; a degeneration of the rigid structure, predominantly observed at low rates of shear and occurring very rapidly at high rates of shear and a reversible apparent thixotropy occurring at high rates of shear that is largely attributable to frictional heating effects.

The occurrence of the pour point in wax bearing mineral oils is considered due to the formation of a rigid network by the solid crystalline components. On shearing these systems the apparent viscosity decreases to a minimum as a regular function of the work of shearing. The structural requirements of pour point depressants as fixed by studies of acrylic polymers are indicated to be an alkyl side chain length of at least 12 carbons and a degree of polymerization commensurate with suitable over-all physical properties. On this basis, polyhexadecylene phthalate was prepared capable of lowering the pour point of an untreated MIL-L-6082A AN-O-8 1100 Grade oil 30°F.

Light microscopical and x-ray diffraction studies of the action of additives on blends of synthetic n-paraffin waxes in dewaxed oil support the thesis that pour point depressants do not enter the crystal lattice but act by means of a surface phenomenon.

Review of the previously reported survey of 835 literature and patent references, as well as the evaluation of commercial additives is given.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDING GENERAL:

M. E. SORTE
Colonel, USAF
Chief, Materials Laboratory
Directorate of Research

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LOW TEMPERATURE LUBRICATING OIL ADDITIVES

I. INTRODUCTION

The problem of producing a lubricant which flows at an ambient temperature of -65° F and has sufficient viscosity for lubrication at aircraft engine working temperatures has become increasingly acute with the expansion of military cold-weather plans. The present project was inaugurated as part of an over-all program for the development of the materials needed. The established objective was the evaluation of the limits of utility of pour point depressants and/or viscosity index improvers with mineral oils, the information acquired to be used if so warranted in the synthesis of new additives, permitting the use of mineral oils under the specified field conditions.

At the inception of this project, there was little or no colligated fundamental information characterizing the additives, the rheological properties of the oils at low temperature, or the effect of the additives on those properties.

Consequently initial work was concerned with thorough review and summary of literature and patent references organized in accordance with their bearing on the general topics of interest. A program was conducted for the analysis of commercially available additives and testing their effectiveness in straight run Pennsylvania and Mid-Continent oils. On the basis of exploratory studies, priorities were established for the various phases of the over-all problems in order to concentrate the effort. The plan developed called for a study of rheological properties of lubricating

oil in the thixotropic region on an absolute basis and the determination of the essential structural features of pour point depressants. These two units were to be coordinated in an interpretation of the mechanism of the pour point depressing process.

II. LITERATURE SURVEY

The following secondary references were used in assembling the bibliography of literature and patents relating to this project:

Chemical Abstracts	1926 to 1949 inclusive
Engineering Index	1930 to 1949 inclusive
Industrial Arts	1930 to 1949 inclusive

The survey[1] is divided into three chapters relating to references of theoretical interest, synthesis of additives, and miscellaneous subjects. Sections and subsections relate to the particular field of application. Within each section references are listed alphabetically according to author. No attempt will be made to re-review in detail the 835 references reported but rather to call attention to highlights.

A. Pour Point Depression

Classification of pour point depressants with regard to molecular structure has been made as follows:

1. Aliphatic-aromatic condensation products - products of Friedel-Crafts condensation of aromatic compounds with chlorinated aliphatics.

2. Condensed olefins - halogen and sulfur treated isobutene polymers.

3. Esters and others - fatty acid esters of lignin, cellulose, glycerol, sorbitol, mannitol, phenol and polyhydric phenol; alkyl ethers and esters of phthaleins and sulfonphthaleins; esters of high molecular weight alcohols with aromatics and alkyl aromatics; condensation products of mono- and polyhydric alcohols with aromatics; polyesters; and metal salts of such ether acids as wax phenoxy benzoic acid.

4. Amines and amides - fatty acid amides and long chained amines.

5. Ketones and aldehydes - products of Friedel-Crafts reactions of acyl halides with petroleum oils and aromatics, haloketones with aromatics, ketones with halides and autocondensation of ketones and aldehydes.

6. Organometallic compounds - metal salts of fatty acids such as aluminum stearate, metal xanthates, bivalent metal sulfonates and metal salts of fatty acid substituted phenols.

7. Oxidation and hydrogenation products - oxidized paraffins and hydrogenated castor oil.

8. Polymers - acrylic polymers, rubber and polyisobutylene derivatives and polymers containing pyrrolidinedione nuclei.

9. Sulfur and phosphorous reaction products - sulfides and polysulfides, sulfurized natural fats and waxes and phosphorous sulfide reaction products such as dithiophosphoric acids.

The outstanding characteristic of the list is the structural diversity of materials effective as pour point depressants. The only consistent feature is a long-chained alkyl group sometimes occurring singly but ordinarily in

multiples. Information regarding the arrangement of these groups is very limited. Of the 291 references to the synthesis of pour point depressants 110 are devoted materials of classification 1. These are principally patents describing the preparation of such additives as Paraflow, Santopour and Pourex. For these cases structure evaluation is impractical since under Friedel-Crafts reaction conditions a variety of condensations and rearrangements can and do occur. The acrylic polymers, for instance, Acryloid 150, offered one of the few examples in which consistent variations might be checked. As addition polymers they consist of simply defined recurring monomer units.

Studies of the mechanism of pour point depression were limited to efforts by Erk[2], by Bondi[3], and by Zimmer, Davis, and Frohlich[4]. Ideas by these men as to the nature of the wax-oil gel giving rise to high pour points and the action of additives on the gel are based largely on qualitative observation. However, the consensus is that the wax component of a wax bearing oil ordinarily crystallizes in a continuous honeycomb structure which prevents flow by trapping the liquid phase. The additive is considered to render the wax incapable of forming the continuous structure.

B. Viscosity Index Improvement

The classes of compounds effective as viscosity index improvers corresponds to those listed for pour point depressants. Indeed some materials serve effectively as both. Viscosity index improvers are indicated to be high molecular weight compounds of the order of 10,000 or more. Those pour point depressants in this molecular weight range appear capable

of functioning as viscosity index improvers.

The bulk of the work on the study of the mechanism of the action of viscosity index improvers has been concentrated on finding a correlation between chemical structures of the additives and their actions. In general, it is believed that the thread-like high polymers, those with straight long paraffinic chains, impart to their solutions a high viscosity index. Repeatedly substantiated studies have revealed that the following are preferentially effective groups:

1. Long paraffinic chains rather than several short chains with an equal number of carbon atoms.

2. Straight chains rather than branched chains.

3. Chains rather than cyclic groups .

4. Cyclic groups at the ends of chains rather than at the centers.

On the other hand, viscosity index improving properties are unaffected by the positions of the chains on the nuclei and by unsaturation in the side chains.

III. COMMERCIAL ADDITIVES

A. Determination of Additive Properties

As an initial phase of experimentation an evaluation of the pour point depressing and viscosity index improving properties of commercial additives was made. Acryloids 150, 710, 722, and HF-600, Paraflows 46X and PDX, Paratone, Pourex, Santopour, Santopours B and C, Santolube 203A, Santodex, high and low molecular weight polybutenes and vinyl ether resin

were tested in Pennsylvania and Mid-Continent bright stocks and 150 viscosity neutral oils, Pennsylvania, Mineral Seal oil, Mid-Continent Cadet Z oil and in blends of two per cent Mid-Continent paraffin match wax, one per cent Mid-Continent microcrystalline wax and one per cent of each of the two waxes with a semi-refined Mid-Continent white oil. Producers of the additives are listed in Table 1. Specifications for the base stocks and the waxes appear in Table 2. ASTM procedures D97-47 and D567-41 were used for all pour point and viscosity index determinations.

1. Pour Point Depression

Tables 3 to 11 summarize the results of the pour point determinations evaluating the depressant actions of the commercial additives which are tabulated in Tables 39 to 174 of Appendix A. Pour points are the minima obtained while additive concentrations are those which yield the maximum depressions. A pour point range of ten degrees is given since the procedure, subject to an experimental error of $\pm$ 5° F, does not distinguish among depressants which are effective in producing pour points within that range. In those cases where more than one concentration of an additive yields the minimum pour point, a concentration range is cited.

In general, no one depressant was more active than others. Of the oils used as base stocks, only the 150 Neutrals were acted upon by small concentrations of additives, while relatively high concentrations of depressants were needed to depress the pour points of Mineral Seal and Cadet Z oils and the synthetic blends. The latter group are light oils containing large percentages of wax. Of special interest is the inability of any of the depressants to markedly depress the pour points of the bright

Table 1

MANUFACTURERS OF COMMERCIAL ADDITIVES

Additive	Manufacturer
Acryloid 150	Rohm and Haas
Acryloid HF 600	Rohm and Haas
Acryloid 710	Rohm and Haas
Acryloid 722	Rohm and Haas
Paratone	Standard Oil Company of New Jersey
Paraflow 46X	Enjay Company
Paraflow PDX	Enjay Company
Pourex	Standard Oil Company of Indiana
Santolube 203-A	Monsanto Chemical Company
Santolube 205	Monsanto Chemical Company
Santolube 570X4	Monsanto Chemical Company
Santolube 394C	Monsanto Chemical Company
Santopour B	Monsanto Chemical Company
Santopour C	Monsanto Chemical Company
Santodex	Monsanto Chemical Company
High Molecular Weight Polybutene	Standard Oil Company of New Jersey
Low Molecular Weight Polybutene	Standard Oil Company of New Jersey
Vinyl Ether Resin	Bakelite Corporation

Table 2

SPECIFICATIONS FOR WAXES AND OILS

Wax Specifications

Wax	Supplier	Base	M.P.(°F)	Oil conc. (wt. %)	Color
1. Paraffin Match Wax	Standard Oil Co. of Indiana	Mid-Continent	120.9	0.87	White
2. Microcrystalline Wax	Bareco Oil Company	Mid-Continent	193.1	-	Amber

Oil Specifications

Oil	Field	Supplier	Cloud Pt. (°F)	Pour Pt. (°F)	Viscosity (SUS) 100°F	210°F	V.I.
White Oil "C"	Mid-Continent	Sinclair	+18	+15	119.8	40.9	95.0
Bright Stock	Pennsylvania	Sinclair	Too dark	+10	2,217.0	148.4	101.0
Bright Stock	Mid-Continent	Mid-Continent Co.	Too dark	+10	2,454.8	149.9	96.5
150 Neutral	Pennsylvania	Sinclair	+14	+10	151.5	43.1	95.0
150 Neutral	Mid-Continent	Mid-Continent Co.	-	-5	164.3	43.9	94.0
Mineral Seal Oil	Pennsylvania	Sinclair	+20	+20	19.4	7.0	-
Cadet Z Oil	Mid-Continent	Sinclair	+20	+26	49.0	32.9	82.0

Table 3

POUR POINT DEPRESSION IN PARAFFIN WAX-WHITE OIL BLEND

Additive	Additive Conc (wt. %)	Pour Point (°F)
Paraflow PDX	3.0 - 15.0	-40 to -50
Santopour B	10.0	-40 to -50
Pourex	3.0 - 10.0	-25 to -35
Santopour C	10.0	-25 to -35
Acryloid 150	0.5	-25 to -35
Santopour	10.0	-25 to -35
Paraflow 46X	0.5 - 15.0	-10 to -20

Table 4

POUR POINT DEPRESSION IN MICROCRYSTALLINE WAX-WHITE OIL BLEND

Additive	Additive Conc. (wt. %)	Pour Point (°F)
Santopour B	10.0	-25 to -35
Pourex	10.0	-25 to -35
Santopour C	10.0	-25 to -35
Paraflow 46X	5.0	-10 to -20
Santopour	1.0 - 5.0	-10 to -20
Paraflow PDX	10.0 - 15.0	-10 to -20

Table 5

POUR POINT DEPRESSION IN MICROCRYSTALLINE-PARAFFIN-WHITE OIL BLEND

Additive	Additive Conc (wt. %)	Pour Point (°F)
Santopour B	3.0 - 10.0	-40 to -50
Paraflow PDX	10.0 - 15.0	-25 to -35
Santopour	3.0	-25 to -35
Pourex	10.0	-25 to -35
Santopour C	10.0	-10 to -20
Paraflow 46X	10.0	-10 to -20
Acryloid 150	1.0 - 15.0	-10 to -20

Table 6

POUR POINT DEPRESSION IN PENNSYLVANIA 150 NEUTRAL OIL

Additive	Additive Conc (wt. %)	Pour Point (°F)
Acryloid 150	0.5 - 3.0	-40 to -50
Paraflow PDX	3.0 - 10.0	-40 to -50
Paraflow 46X	3.0	-40 to -50
Santopour B	3.0 - 10.0	-40 to -50
Santopour	3.0	-40 to -50
Pourex	10.0	-40 to -50
Acryloid 722	10.0	-40 to -50
Santopour C	1.0 - 3.0	-25 to -35

Table 7

POUR POINT DEPRESSION IN MID-CONTINENT 150 NEUTRAL OIL

Additive	Additive Conc (wt. %)	Pour Point (°F)
Paraflow PDX	3.0	-40 to -50
Santopour	1.0 - 3.0	-25 to -35
Paraflow 46X	1.0 - 3.0	-25 to -35
Acryloid 150	1.0 - 3.0	-25 to -35
Santopour B	1.0 - 3.0	-25 to -35
Santopour C	1.0 - 10.0	-25 to -35
Pourex	3.0	-25 to -35
Acryloid 722	10.0	-25 to -35

Table 8

POUR POINT DEPRESSION IN PENNSYLVANIA BRIGHT STOCK

Additive	Additive Conc (wt. %)	Pour Point (°F)
Paraflow PDX	3.0 - 10.0	-10 to -20
Santopour	3.0 - 10.0	-10 to -20
Santopour C	3.0	-10 to -20
Santopour B	10.0	-10 to -20
Acryloid 722	1.0 and 10.0	-10 to -20
Acryloid 150	1.0 - 10.0	.0 to -5
Pourex	3.0 - 10.0	0 to -5

Table 9

POUR POINT DEPRESSION IN MID-CONTINENT BRIGHT STOCK

Additive	Additive Conc. (wt. %)	Pour Point (°F)
Acryloid 150	1.0 - 3.0	-10 to -20
Santopour	10.0	-10 to -20
Santopour B	10.0	-10 to -20
Santopour C	5.0	-10 to -20
Paraflow PDX	10.0	-10 to -20
Pourex	10.0	-10 to -20
Paraflow 46X	1.0 -10.0	0 to -5

Table 10

POUR POINT DEPRESSION IN PENNSYLVANIA MINERAL SEAL OIL

Additive	Additive Conc. (wt. %)	Pour Point (°F)
Santopour B	10.0	-10 to -20
Pourex	10.0	0 to -5

Table 11

POUR POINT DEPRESSION IN CADET Z OIL

Additive	Additive Conc (wt. %)	Pour Point (°F)
Santopour B	10.0	-40 to -50
Paraflow 46X	3.0	-10 to -20
Pourex	10.0	-10 to -20
Paraflow PDX	3.0 - 10.0	0 to -5
Acryloid 150	3.0	0 to -5

stocks. While the relative depressant activities of the commercial products are listed in Table 12, there appears to be little basis for distinguishing among their effectiveness. Number "1" indicates maximum depression, while number "3" is minimum. Whereas Santopour B is consistently most active, it must be recognized that in most cases concentrations as high as ten per cent are necessary for optimum depression.

2. Viscosity Index Improvement

The order of the effectiveness of additives as viscosity index improvers in the test oils is tabulated in Table 13. Complete data are presented in Appendix A. In compiling Table 13 the additives were assigned numbers from 1 to 10 in order of their effectiveness. For example, the additive causing the greatest increase in viscosity index per unit concentration in Pennsylvania 150 Neutral was Acryloid HF-600. This was assigned the number 1. In contrast to this the vinyl ether resin was given the number 10 since it had the least effect on this oil.

In the synthetic wax-white oil blends, Acryloid HF-600 proved to be the most effective and Santodex the least effective of the viscosity index improvers. Santopour C gave satisfactory results in all cases. Paratone as well as the vinyl ether resin was somewhat effective in all blends, while the polybutenes were intermediate with the microcrystalline wax blend.

In both Pennsylvania and Mid-Continent Bright Stocks and 150 Neutral oils Acryloid HF-600 also gave the best results. However, no large increase in viscosity index was observed in the Bright Stocks.

Table 12

COMPARISON OF ADDITIVES AS POUR POINT DEPRESSANTS

Additive	Synthetic Wax-Oil Blend			150 Neutral Oils		Bright Stock			
	Paraffin Wax	Microcrystalline Wax	Paraffin & Microcrystalline Wax	Pennsylvania	Mid-Continent	Pennsylvania	Mid-Continent	Pennsylvania Mineral seal	Cadet Z
Acryloid 150	2	-	3	1	2	2	1	-	3
Acryloid 722	-	-	-	1	2	1	-	-	-
Santopour	2	2	2	1	2	1	1	-	-
Santopour B	1	1	1	1	2	1	1	1	1
Santopour C	2	1	3	2	2	1	1	-	-
Paraflow 46X	3	2	3	1	2	-	2	-	2
Paraflow PDX	1	2	2	1	1	1	1	-	3
Pourex	2	1	2	1	2	2	1	2	2

Table 13

COMPARISON OF ADDITIVES AS VISCOSITY INDEX IMPROVERS

Additive	Synthetic Wax-Oil Blend			150 Neutral Oils		Bright Stock		Pennsylvania Mineral Seal	Cadet Z
	Paraffin Wax	Microcrystalline Wax	Paraffin & Microcrystalline Wax	Pennsylvania	Mid-Continent	Pennsylvania	Mid-Continent		
Acryloid 150	4	8	8	2	3	9	7	4	3
Acryloid 722	5	6	6	8	2	4	3	5	4
Acryloid HF-600	1	1	1	1	1	1	1	2	1
Acryloid 710	2	5	5	4	4	3	2	3	2
Santodex	8	10	10	5	5	2	4	1	5
Santopour C	3	4	4	7	6	5	5	8	9
Paratone	7	7	7	6	7	6	6	10	6
Low Mol. Wt. Polybutene	10	3	3	9	8	7	8	6	7
High Mol. Wt. Polybutene	9	2	2	10	9	8	9	7	8
Vinyl ether Resin	6	9	9	3	10	10	10	9	10

In both the Pennsylvania Mineral Seal oil and the Mid-Continent Cadet Z oil, the relative arrangement of the additives in order of effectiveness was identical except for the greater activity of Santodex in the Pennsylvania oil. Since Pennsylvania Mineral Seal oil had an initial viscosity index 21.7 units greater than the Mid-Continent Cadet Z oil, the viscosity indices must be expected to be higher for the Pennsylvania oil. In addition, the variation in viscosity index between the two oils became greater with higher concentrations of additive.

In general, the effectiveness of the additives is dependent upon the type of composition and original viscosity index of the oil. Acryloid HF-600 was consistently among the most effective additives. In all cases, the largest increase in viscosity index was observed with the lower viscosity oils.

B. Analysis of Commercial Additives

Analyses of commercial additives were carried out to supplement and substantiate conclusions drawn from the literature survey as to the compositions and structures of active pour point depressants and viscosity index improvers. Qualitative determinations of elements were made by sodium fusion analyses and of functional groups by infrared spectroscopy. In the case of the Acryloids, which are basically acrylic polymers, saponification equivalents were measured to indicate the monomer molecular weight. Polymer molecular weights were determined to provide an approximate measure of molecular size. Study of commercial additives was complicated by the necessity to isolate them by extraction from the oil solutions in which they are marketed.

1. Isolation of Commercial Additives

Commercial additives are sold as concentrated solutions in mineral oil. Analysis, therefore, necessitated separation from this solution. Since the additive molecular weight was considerably greater than the oil, a partial precipitation method from a third solvent was adopted for this purpose. The procedure used is given in Appendix B. The additive concentrations listed in Table 14 are the results of two extractions yielding duplicate results as determined by additive concentration in the commercial blend and additive average molecular weight. The solubility of extracted additive in the raffinate provides an indication of the degree of inaccuracy in the results, Table 14. This measure of the weight per cent of the total additive retained by the solvent layer in each separation approximates the inclusion of additive in the oil fraction.

Among the analyses to be subsequently described, only the determination of average molecular weight is dependent upon the isolation of a quantitative yield of additive. Infrared spectral and elemental analyses and the determination of the saponification equivalent require only that a representative oil-free sample of material be obtained.

2. Elemental Analysis

The elemental analyses of the additive concentrates for sulfur, nitrogen and halogen were carried out according to a sodium fusion procedure[5]. Data presented in Table 15 shows that the only positive test was for sulfur in Santolube 203A. Flame tests have indicated that that compound probably contains barium.

Table 14

EXTRACTIONS OF ADDITIVES

Additive	Solvent Precipitant	Additive Recovered (Wt.% Average)	Oil Recovered (Wt.% Average)	Additive in Raffinate (Wt.% Average)
Acryloid 150	Diethyl ether Absolute ethanol	42.1	56.5	-
Acryloid 710	Diethyl ether Absolute ethanol	32.8	62.6	2.6
Acryloid 722	Diethyl ether Absolute ethanol	38.6	59.0	2.2
Acryloid HF-600	Diethyl ether Absolute ethanol	24.4	72.9	0.82
Santopour	Diethyl ether Absolute ethanol	9.1	89.9	-
Santopour B	Petroleum ether Absolute ethanol	10.2	89.8	-
Santolube 203A	Petroleum ether Absolute ethanol	21.0	77.1	-
Esso High Molecular Weight Polybutene	Petroleum ether Absolute ethanol	27.7	70.3	4.3
Esso Low Molecular Weight Polybutene	Petroleum ether Absolute ethanol	33.5	63.6	0.38
Paratone	Diethyl ether Absolute ethanol	33.2	65.9	1.4
Paraflow 46X	Diethyl ether Absolute ethanol	31.5	68.4	-
Paraflow 46X	Diethyl ether sec.-Amyl alcohol	9.8	89.4	-
Paraflow PDX	Diethyl ether Absolute ethanol	31.1	68.7	-
Pourex	Diethyl ether Absolute ethanol	9.3	88.6	-
Santodex	Diethyl ether Absolute ethanol	16.6	83.4	1.0
Santopour C	Diethyl ether Absolute ethanol	32.6	62.5	0.8

Table 15

ELEMENTAL ANALYSIS OF ADDITIVES

Additive	Appearance of Crude Additive	Analysis for Elements		
		Nitrogen	Sulfur	Chlorine
Santolube 203A	Dark brown jelly-like solid	-	+	-
Santopour	Dark brown viscous liquid	-	-	-
Santopour B	Dark brown viscous liquid	-	-	-
Paraflow PDX	Dark brown viscous liquid	-	-	-
Paraflow 46X	Dark brown viscous liquid	-	-	-
Pourex	Dark brown viscous liquid	-	-	-
Santodex	Soft, sticky, light brown, clear solid	-	-	-
Paratone NL4	Soft, sticky, clear solid	-	-	-
Polybutene Low M. W.	Soft, sticky, clear solid	-	-	-
Polybutene High M. W. .	Soft, sticky, slightly yellow, clear solid	-	-	-
Acryloids	Very soft to hard, sticky rubbery, amber colorless solid	-	-	-

3. Infrared Analysis

Table 16 lists the functional groups present in the series of additives as evidenced by infrared absorption. Those materials which are believed to be products of Friedel-Crafts reactions of chlorinated paraffin wax and aromatics (Santopour, Santopour B, Santopour C, Paraflow PDX, Paraflow 46X, and Pourex) display the presence of long alkyl substituted aromatic groups, while all of that series other than Paraflow PDX also have a carbonyl absorption peak. The Acryloids are believed to be acrylic polymers with unsaturated and carbonyl groups. Finally, Paratone and high and low molecular weight polybutenes which display t-butyl and unsaturation peaks are most likely polyisobutylenes.

4. Saponification of Acryloids

The saponification equivalents of the Acryloids were determined to establish the ester chain length of the monomeric units of the respective acrylic polymers. A saponification equivalent of an ester, g of unknown/g equivalent of KOH is equal to the equivalent weight of the ester group. In the case of a polymer composed of monomer units having a single ester group, it is the molecular weight of the monomer.

The determination of the saponification equivalent of a polymeric material is incumbent upon complete reaction of all ester groups. Due to low solubility and steric hindrance within the molecule, complete saponification is dependent upon vigorous reaction conditions. Since the experimental procedure involves titration of excess alkali, the use of concentrated solutions of base such as Claisen's alkali, yielded results which were not precise and which were subject to experimental errors beyond

Table 16

GROUPS IDENTIFIABLE BY INFRARED ABSORBANCE

Additive	t-Butyl	Unsaturated	Long Alkyl Substituted Aromatic	Sulfonic Acid	Aromatic	Carbonyl
Acryloid 150	-	+	-	-	-	+
Acryloid HF-600	-	+	-	-	-	+
Acryloid 710	-	+	-	-	-	+
Acryloid 722		+	-	-	-	+
Santodex	-	-	+	-	+	-
Santopour	-	+	+	-	+	+
Santopour B	-	+	+	-	+	+
Santopour C	-	-	+	-	+	+
Santolube 203A	-	+	+	+	+	-
Paraflow PDX	-	-	+	-	+	-
Paraflow 46X	-	-	+	-	+	+
Paratone	+	+	-	-	-	-
Polybutenes	+	+	-	-	-	-
Pourex	-	-	+	-	+	+

acceptable limits. The use of diethylene glycol, benzene and pyridine as solvents also gave unsatisfactory results. In an effort to produce molecules of sufficiently low molecular weight to be readily soluble in available reagents, attempts were made to thermally depolymerize Acryloid 150 by a method successful with synthetic lauryl polymethacrylate; however, the results indicated that uncontrolled degradation of the ester probably had occurred.

Consistent saponification equivalents were obtained with the use of petroleum ether (b.p. 65-110°C) as solvent and a three normal ethanolic solution of potassium hydroxide as saponification base. These experimental conditions were used in the analysis of the four principal Acryloids. Results are listed in Table 17.

The saponification equivalent of 256 for Acryloid 150 indicates that the additive may be either dodecyl polymethacrylate or tridecyl polyacrylate. In view of the lack of a commercial source for tridecyl alcohol, it appeared most likely that Acryloid 150 is the dodecyl polymer. The data also indicates that Acryloid 722 is octyl polymethacrylate. The high saponification equivalents for Acryloid 710 and HF-600 suggest that either saponification was not complete or that they are acrylic copolymers.

5. Molecular Weights of Additives

The accurate determination of the molecular weight of commercial additives is dependent upon the quantitative isolation of the concentrates from the marketed oil solutions. As has been previously indicated, such a separation was not accomplished. As a consequence, data given in Table 18 are approximations and are indicative only of the ranges of molecular weights. The ebullioscopic method[6] used in the determinations is

Table 17

SAPONIFICATION OF ACRYLOIDS IN PETROLEUM ETHER

Additive	Calculated For Lauryl Methacrylate	Saponification Equivalent (g/g equiv. KOH)
Acryloid 150	254	252
Acryloid 710	254	318
Acryloid 722	254	224
Acryloid HF-600	254	429

Table 18

AVERAGE MOLECULAR WEIGHTS OF COMMERCIAL ADDITIVES

Additive	Average Molecular Weight*
Acryloid 150	4400
Acryloid 710	7000
Acryloid 722	5200
Acryloid HF-600	7000
Paraflow 46X	2200
Paraflow PDX	1600
Pourex	3350
Santodex	4000
Santopour C	7000
Santopour	5500
Santopour B	450
Santolube 203A	3600
Paratone	3600

*Ebullioscopic

subject to limitations resulting from the restriction to the use of dilute solutions. As a result of this restriction, it was found empirically that molecular weights in the vicinity of 7,000 are the maxima yielding measurable increments in boiling point elevation. However, as will be subsequently indicated, the use of this procedure for the determination of molecular weights above 1,500 is still further subject to discrepancies as evidenced by comparisons with values determined cryoscopically.

6. Summation of Analyses of Commercial Additives

Combining the results of the literature survey with those of the analyses described in this section, the following compositions may be suggested for commercial additives:

Acryloid 150 - Dodecyl polymethacrylate, average molecular weight approximately 4,500.

Acryloid 710 - Acrylic polymer of undetermined composition, average molecular weight approximately 7,000.

Acryloid 722 - Octyl polymethacrylate or polyacrylate (most likely 2-ethylhexyl), average molecular weight approximately 5,000.

Acryloid HF-600 - Acrylic polymer of undetermined composition, average molecular weight approximately 7,000.

Paraflow 46X - Product of a Friedel-Crafts reaction of naphthalene, chlorinated wax and an acyl chloride, approximate average molecular weight 2,000.

Paraflow PDX - Product of a Friedel-Crafts reaction of naphthalene and chlorinated wax, average molecular weight approximately 1,500.

Pourex - Product of a Friedel-Crafts reaction of chlorinated wax and undetermined aromatic, contains carbonyl, average molecular weight approximately 3,500.

Santodex - Polymeric hydrocarbon, possibly alkylated styrene, average molecular weight approximately 4,000.

Santopour C - Probable product of a Friedel-Crafts reaction, displays presence of long-chain alkyl, aromatic and carbonyl group, average molecular weight approximately 7,000.

Santopour B - Possible monobasic ester of aromatic acid and wax phenol, average molecular weight approximately 450.

Santopour - Product of the reaction of chlorinated wax, phenol and phthaloyl chloride, approximate molecular weight 5,500.

Santolube 203A - Barium salt of an organic sulfonic acid, approximate molecular weight 3,500.

Paratone - Polyisobutene, approximate molecular weight 3,500.

IV. DETERMINATION OF ESSENTIAL FEATURES OF POUR POINT DEPRESSANTS

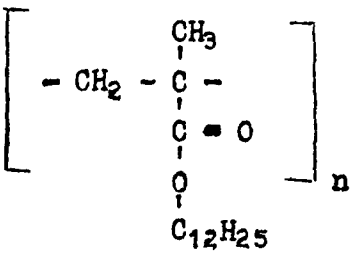
Structural studies of the essential features of pour point depressants were initiated on acrylic polymers because they comprise one group of known additives, the Acryloids. Of the widely used depressants Acryloid 150 alone is a simple addition polymer. As such its structure may be defined in terms of the monomer structure and the number of monomer units, the degree of polymerization, making up the polymer. Work was begun with dodecyl polymethacrylate because it was indicated by analysis to be the active principle of Acryloid 150. Subsequent trial showed indeed that dodecyl polymethacrylate was effective as a pour point depressant. The two points of study of the generalized acrylic polymer structure illustrated in

Figure 1 were:

1. The effect of the variation in n, the degree of polymerization on dodecyl polymethacrylate additive properties.

2. The effect of variation in ester chain length on the additive properties of acrylic and methacrylic polymers.

Figure 1



DODECYL POLYMETHACRYLATE

A. Dodecyl Polymethacrylate-Pour Point Depression of Pennsylvania Straight Run Oils as a Function of Average Degree of Polymerization

A study of the influence of the degree of polymerization of dodecyl polymethacrylate on its activity as a pour point depressant was carried out using three Pennsylvania base stocks, Mineral Seal, 150 Neutral and Bright Stock, the properties of which are recorded in Table 2. The use of different oil fractions derived from the same field and dewaxed to the same pour point provided a basis for evaluating the role of the molecular weight of the base stock. Preparations of polymers were carried out with the use of chain transfer agents to enable variation of molecular weight.

1. Preparation of Polymers

a. Control of Degree of Polymerization with Chain Transfer Agents

Figure 2
MECHANISM OF ADDITION POLYMERIZATION

Initiation:

$$RCOOCR \rightarrow 2RCO\cdot$$

$$RCO\cdot \rightarrow R\cdot + CO_2$$

$$R\cdot + CH_2{=}CHX \rightarrow RCH_2CHX\cdot$$

Propagation:

$$RCH_2CHX\cdot + n(CH_2{=}CHX) \rightarrow R(CH_2CHX)_{n+1}\cdot$$

Termination:

$$2R(CH_2CHX)_{n+1}\cdot \rightarrow R(CH_2CHX)_{2n+2}R$$

$$2R(CH_2CHX)_{n+1}\cdot \rightarrow R(CH_2CHX)_{n+1}H + R(CH_2CHX)_nCH{=}CHX$$

The use of chain transfer agents provides an additional means of chain termination. The concept of chain transfer as introduced by Flory[7] may be exemplified by the illustration in Figure 3 as applied to the polymerization of mono-olefinic monomers, such as the acrylates, carbon tetrachloride serving as the chain transfer agent.

Figure 3
CHAIN TRANSFER CONCEPT

$$R(CH_2CHX)_{n+1}\cdot + CCl_4 \rightarrow R(CH_2CH)_{n+1}Cl + CCl_3\cdot$$

$$CCl_3\cdot + CH_2{=}CHX \rightarrow CCl_3CH_2CHX\cdot$$

It is apparent from the example cited that the process of chain transfer does not affect the growth process of the polymer chain, but merely increases the rate of termination.

The use of carbon tetrachloride, chloroform and bromotrichloromethane as chain transfer agents has been reported by Mayo and his coworkers[8] and the application of these materials on this project for the control of the polymerization of dodecyl methacrylate is largely an extension of their findings.

Benzoyl peroxide was used exclusively as polymerization catalyst in a one molar per cent concentration at reaction temperatures ranging from 70° C for high molecular weight product to 90° C for low molecular weights. Ordinarily the transfer agent was present in sufficient concentration to preclude the use of a solvent for efficient heat transfer; however, at low concentrations of chain transfer agent more consistent results were obtained with the use of an inert solvent such as benzene.

The final reaction product was examined in several ways depending primarily upon the stage of development of the method. Materials were obtained from the bulk polymerization of dodecyl methacrylate that were insoluble in lubricating oil or common organic solvents. Consequently, the products from initial experiments with chain transfer agents were tested simply for solubility in high boiling petroleum ether. These data were checked by ebullioscopic molecular weight determinations of the crude products. In a further refinement, the crude polymer was fractionally precipitated from benzene solution by the gradual addition of methyl alcohol and graded into three separate fractions in the order in which they precipitated. The bulk of the polymer appeared in Fraction 2. Fraction 1,

the highest molecular weight material, ordinarily did not consist of more than a few per cent of the total product, and Fraction 3 consisted principally of unreacted monomer.

The summarized results from this series of experiments are reported in Tables 19, 20, and 21. It will be noted that the chain transfer agents are designated as CTA and the monomeric dodecyl methacrylate as M. The molecular weights determined ebullioscopically were subject to correction as determined by the subsequent application of the cryoscopic procedure.

b. Determination of Molecular Weight

Two methods were used for the determination of molecular weights of polymers. The ebullioscopic procedure mentioned previously in determinations of the molecular weights of commercial additive concentrates was first applied to the acrylic polymers. However, as previously stated, the weight concentration of solute in benzene required to obtain a satisfactory boiling point increment was too high for polymeric materials having molecular weights of approximately 7,000 or greater. Moreover, the particular polymers under study caused foaming which made accurate temperature measurement difficult.

The procedure finally adopted was based upon the freezing point lowering of sym-difluorotetrachloroethane. Bernstein and Miller[9] have suggested the applicability of this material as a cryoscopic solvent. For present purposes it proved to be ideal. Its molal freezing point depression constant, determined with di-(2-ethylhexyl) sebacate is 43.4°C/(mole of solute) (1,000 g of solvent). All of the polymers under study were easily

Table 19

POLYMERIZATION OF DODECYL METHACRYLATE (M)

Effect of Chloroform on the Molecular Weight

			Fraction 2	
CTA:M (moles/mole)	Reaction Temp.(°C)	Crude Polymer Av. mol. wt.	Average* mol. wt.	Yield (wt. %)
10	90	1700	-	-
10	65	-	$>$7000	80
20	90	800	2300	60
20	65	-	$>$7000	80

*Ebullioscopic

Table 20

POLYMERIZATION OF DODECYL METHACRYLATE

Effect of Carbon Tetrachloride on the Molecular Weight

				Fraction 2	
CTA:M (moles/mole)	Reaction Temp. °C	Sol. in Pet. Ether	Crude Polymer Av. mol. wt.*	Average mol. wt.*	Yield (wt. %)
0.5	70	insol.	-	-	-
1	70	insol.	-	-	-
2	70	sol.	>7000	-	-
4	70	sol.	-	-	-
6	70	sol.	5545	-	-
10	70	sol.	5545	-	-
10	70	sol.	2250	>7000	52
20	70	sol.	628	>7000	15

*Ebullioscopic

Table 21

POLYMERIZATION OF DODECYL METHACRYLATE (M)

Effect of Bromotrichloromethane on the Molecular Weight

			Fraction 2	
CTA:M (moles/mole)	Benzene:M (moles/mole)	Reaction Temp.(°C)	Average mol. wt.*	Yield (wt. %)
2	5	90	750	90
2	0	90	850	48
1	5	90	1100	90
1	0	90	1100	72
0.2	5	90	3100	51
0.1	5	90	4400	52

*Ebullioscopic

soluble at the freezing point, 24°C. Moreover, this low freezing point precluded the possibility of degradation of the solute during the determination.

The apparatus used for the molecular weight determinations had a standard design. It would appear that in view of the proximity of the freezing point to room temperature, only reasonable care would be required in the insulation of the freezing point apparatus. However, this was found not to be true. As an inverse function of its large molal freezing point depression constant, sym-difluorotetrachloroethane has a very low heat of fusion, which makes it necessary to exert considerable care to control supercooling and the maintenance of adiabatic conditions. A description of the equipment and experimental procedure may be found in Appendix B.

The molal freezing point constant of 43.4°C readily facilitated determinations of molecular weights in the range of 14,000 with a precision of two per cent. Consequently, results of cryoscopic measurements are given priority over those determined ebullioscopically. A comparison of average molecular weights determined cryoscopically with those previously determined ebullioscopically is presented in Table 22. In the following sections polymers will be referred to by the code number designated in the table.

An independent check of the cryoscopic method was made in an exhaustive fractionation of dodecyl polymethacrylate to be described in a later section. When a sample of the polymer having a cryoscopic average molecular weight of 4,000 was fractionated into eleven components, the weighted average of the molecular weights of the fractions, also determined cryoscopically, was equal to the average molecular weight of the

Table 22

COMPARISON OF EBULLIOSCOPIC AND CRYOSCOPIC AVERAGE MOLECULAR WEIGHTS OF DODECYL POLYMETHACRYLATE

Chain Transfer Agent	CTA/M*	Code No.	Average Molecular Weight	
			Ebullioscopic	Cryoscopic
Bromotrichloromethane	2	DPM-1	850	850
Bromotrichloromethane	1	DPM-2	1100	1100
Chloroform	20	DPM-3	2300	2000
Bromotrichloromethane	0.1	DPM-4	4400	3000
Carbon Tetrachloride	20	DPM-5	>7000	3700
Carbon Tetrachloride	2	DPM-6	>>7000	4000

*Moles of chain transfer agent: mole of monomer

mother polymer. As a result, cryoscopic molecular weights will be cited in the subsequent discussion of the effect of that factor on the pour point depressing action of dodecyl polymethacrylate.

2. Effect of Polymer Molecular Weight on the Pour Point Depressing Action in Pennsylvania 150 Neutral Oil

The dependence of pour point depression of Pennsylvania 150 Neutral oil on the molecular weight and concentration of dodecyl polymethacrylate is shown in Figure 4. It should be emphasized that these curves are based upon bulk polymers with only unreacted monomer removed. Each sample comprised a molecular weight range the breadth of which appeared to vary directly with the average molecular weight observed. Thus, DPM-5 and DPM-6 contain fractions similar to DPM-4, DPM-3, DPM-2, and DPM-1. DPM-1 and DPM-2, on the other hand, contain no high molecular weight fractions. In addition, the data are subject to the usual objections of pour point determinations and cannot be warranted to a greater accuracy than $\pm$ 5° F.

Nevertheless, several valuable conclusions can be drawn. The marked pour depressing effect of the higher molecular weight materials is clearly shown. For example, a concentration of 0.1 per cent of DPM-6 was sufficient to cause a pour point of -28° F while six per cent of DPM-4 was needed to effect the same depression. If the term "pour point depressant" is to be reserved for those materials having a very marked influence on the properties of lubricating oil in low concentration, then DPM-2 and DPM-1 cannot be so classified. It hardly seems reasonable to attribute the observed depressions at concentrations of 30 per cent to any unusual or special property. It is possible, for instance, that the wax solubility was increased

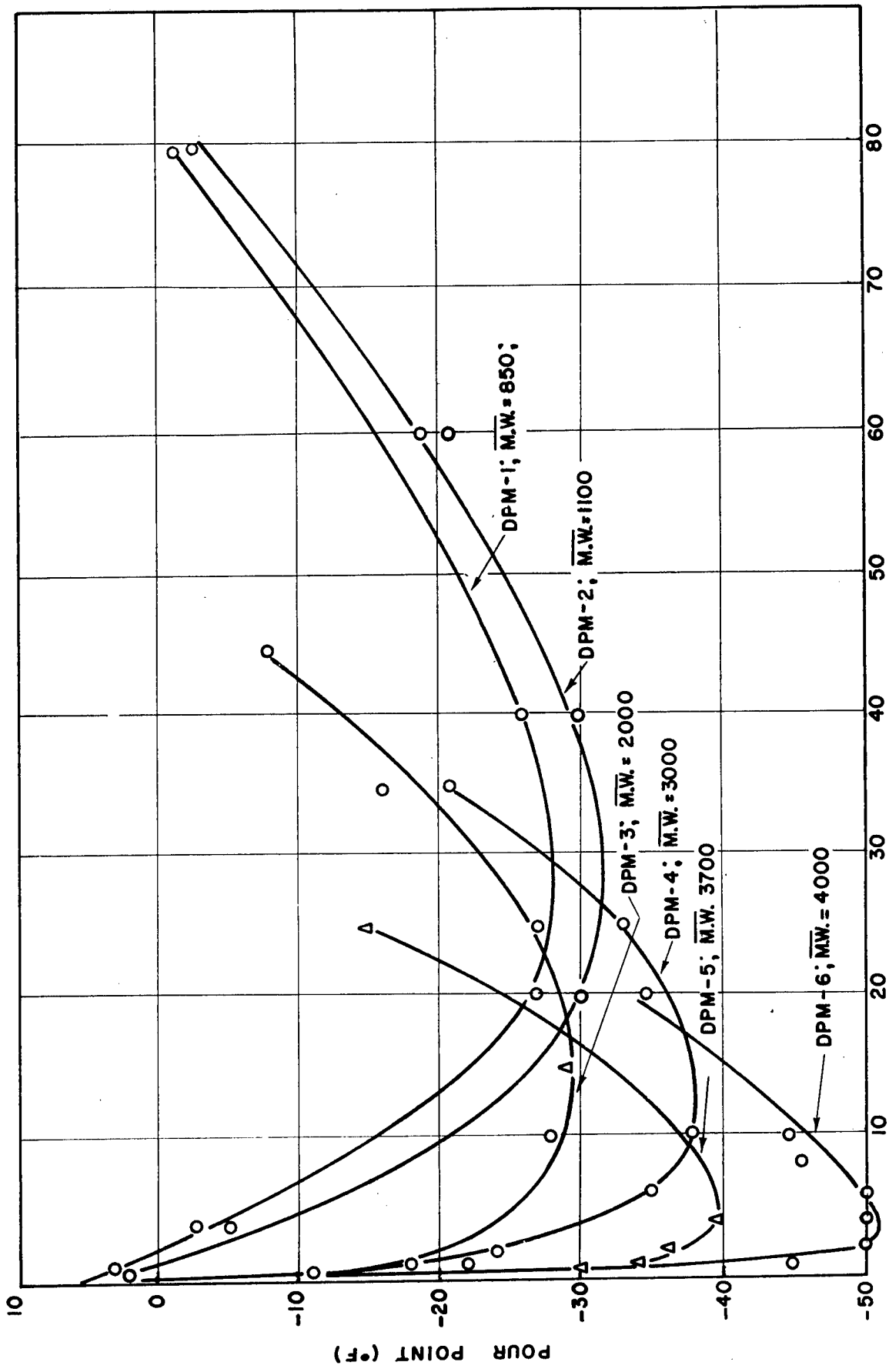


FIG. 4 —DODECYL POLYMETHACRYLATE-ADDITIVE PROPERTIES IN PENNSYLVANIA 150 NEUTRAL OIL AS A FUNCTION OF DEGREES OF POLYMERIZATION.

sufficiently to prevent the process of wax-oil gelation from occurring.

In order to overcome the limitations resulting from the use of polymers with wide molecular weight distributions, dodecyl polymethacrylate samples having relatively narrow molecular weight ranges have been prepared by the exhaustive fractionation of a polymer having a cryoscopic average molecular weight of 4,000. The fractionation was carried out according to the scheme presented in Figure 5 and the experimental procedure reported in the Appendix B. The data are consolidated in Table 23.

The three highest molecular weight fractions isolated, 8,000, 10,000 and 14,000, have each been tested for pour point depressant activity in Pennsylvania 150 Neutral oil. The results, given in Figure 6 and Table 24, disclose no important differences among the actions of the three fractions and the unfractionated polymer within the experimental accuracy of the ASTM method for pour point determination, $\pm$ 5° F.

It is significant that the unfractionated dodecyl polymethacrylate, containing a relatively low concentration of high molecular fractions, had an activity equivalent to or higher than that of an equal concentration of the high molecular weight polymer. It is possible that the low molecular weight fractions, although ineffective as depressants, may exert a synergistic action.

3. Effect of Polymer Molecular Weight on Pour Point Depressing Action in Mineral Seal Oil

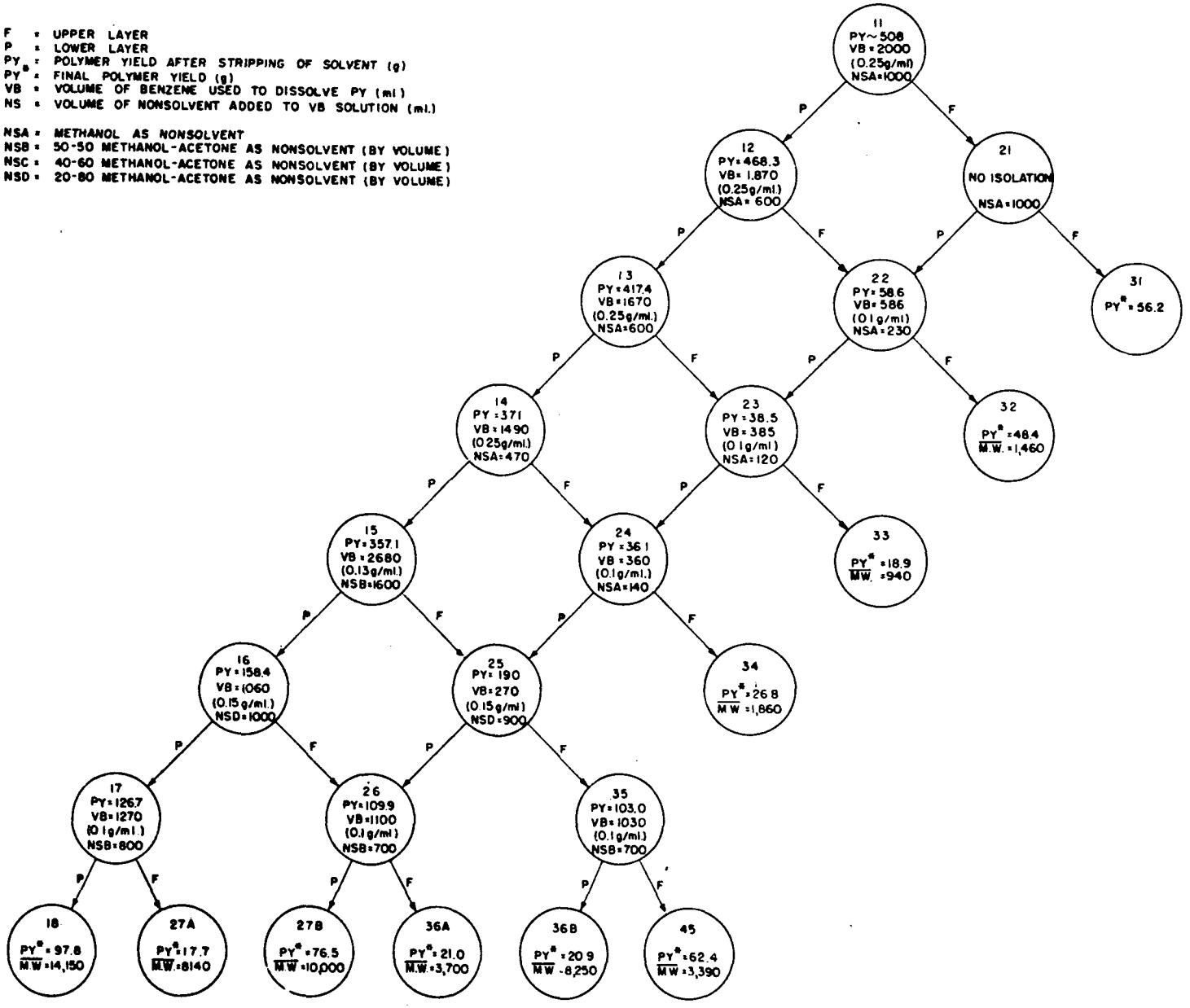
The use of Mineral Seal oil to determine the relationship of additive molecular weight to depression activity has demonstrated that pour

FIGURE 5

SCHEME FOR FRACTIONATION OF DODECYL POLYMETHACRYLATE, AVERAGE MOLECULAR WEIGHT 4000

F = UPPER LAYER
P = LOWER LAYER
PY_s = POLYMER YIELD AFTER STRIPPING OF SOLVENT (g)
PY^* = FINAL POLYMER YIELD (g)
VB = VOLUME OF BENZENE USED TO DISSOLVE PY (ml)
NS = VOLUME OF NONSOLVENT ADDED TO VB SOLUTION (ml.)

NSA = METHANOL AS NONSOLVENT
NSB = 50-50 METHANOL-ACETONE AS NONSOLVENT (BY VOLUME)
NSC = 40-60 METHANOL-ACETONE AS NONSOLVENT (BY VOLUME)
NSD = 20-80 METHANOL-ACETONE AS NONSOLVENT (BY VOLUME)



WADC TR 53-11

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Table 23

COMPOSITION OF BULK DODECYL POLYMETHACRYLATE PREPARED IN CARBON TETRACHLORIDE SOLUTION

(Molar Ratio of Solvent to Monomer = 2/1)

Molecular Weight*	Weight (g)	Moles	Concentration (wt. %)	Concentration (Mol. %)
14000 or greater	97.8	0.007	22.4	2.1
10000 - 14000	76.5	0.008	17.5	2.4
8000 - 10000	38.6	0.005	8.9	1.5
3000 - 8000	72.9	0.021	16.6	6.3
1000 - 3000	75.2	0.047	17.2	14.1
250 - 1000	18.9	0.020	4.3	6.0
250	56.2	0.225	12.9	67.6
	436.1	0.333		

*Cryoscopic

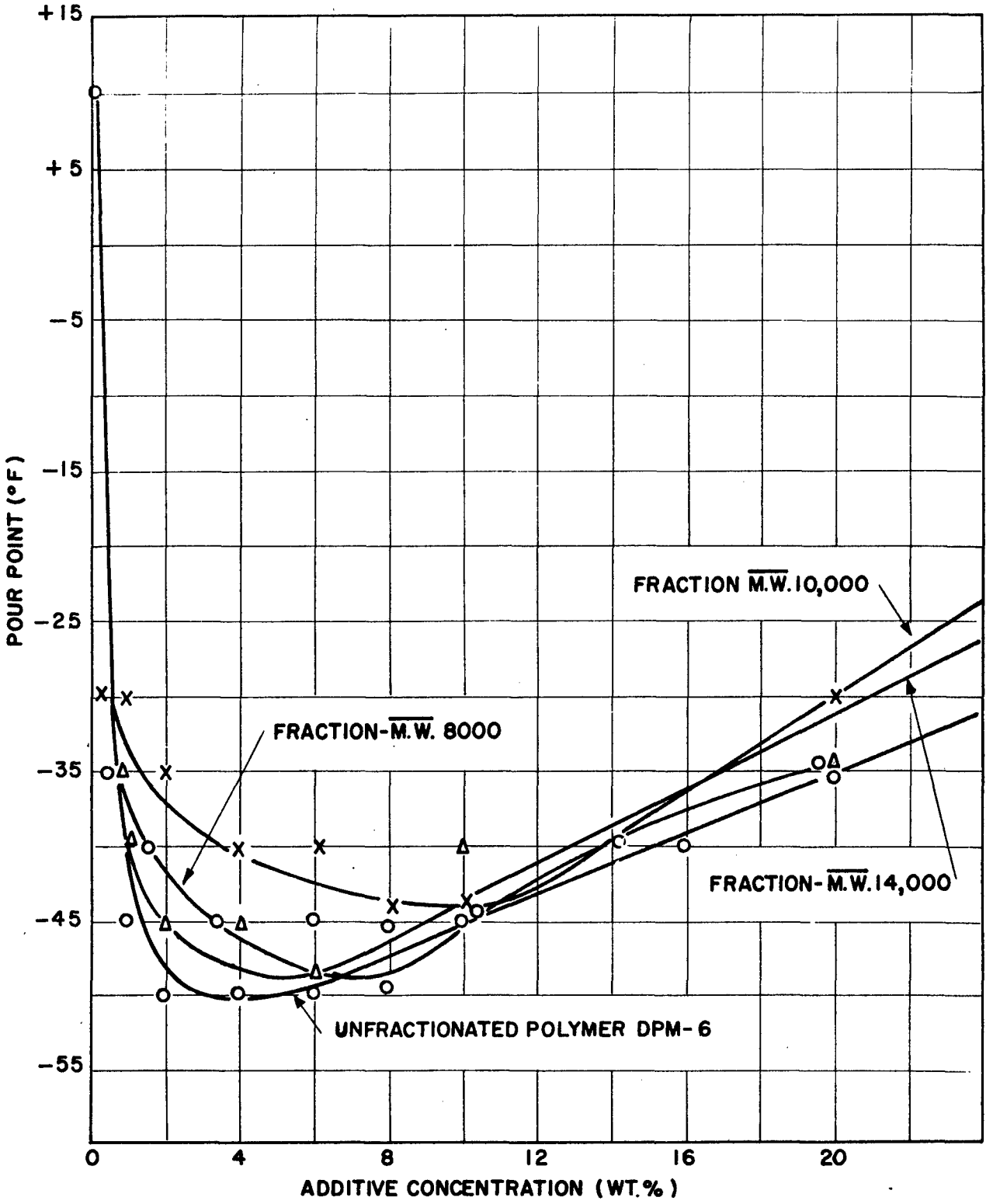


FIG. 6 - POUR DEPRESSION OF EXHAUSTIVELY FRACTIONATED DODECYL POLYMETHACRYLATE IN PENNSYLVANIA 150 NEUTRAL OIL

Table 24

POUR POINTS AND VISCOSITIES OF EXHAUSTIVELY FRACTIONATED DODECYL POLYMETHACRYLATE--PENNSYLVANIA 150 NEUTRAL OIL BLENDS

Additive Molecular Weight	Additive Conc. (wt.%)	Pour Point (°F)	Viscosity 100° F Centistokes	100° F SUS	210° F Centistokes	210° F SUS	Viscosity Index
4000*	20.0	-35					
	16.0	-40					
	14.0	-40					
	10.0	-45					
	8.0	-45					
	6.0	-50					
	4.0	-50					
	2.0	-50					
	1.0	-45					
	0.5	-35					
	0.05	+10					
14000*	20.0	-35	698.0	3224.7	102.3	475.9	>130
	10.0	-40	212.0	979.4	33.4	157.1	138
	8.0	-40	159.0	734.6	25.4	121.5	140
	6.0	-50	115.0	531.3	18.7	92.71	142
	4.0	-45	79.4	366.8	12.8	69.34	141
	2.0	-45	53.4	247.0	8.56	54.28	134
	1.0	-40	42.5	197.0	6.81	48.43	123
	0.5	-35	37.1	172.6	6.22	46.53	123
10000**	20.0	-30					
	10.0	-45					
	8.0	-45					
	6.0	-40					
	2.0	-35					
	1.0	-30					
	0.5	-30					
8000**	20.0	-40					
	10.0	-45					
	8.0	-50					
	6.0	-45					
	3.5	-45					
	1.75	-40					
	0.8	-30					

* Unfractionated polymer - cryoscopic
** Exhaustively separated fractions of*

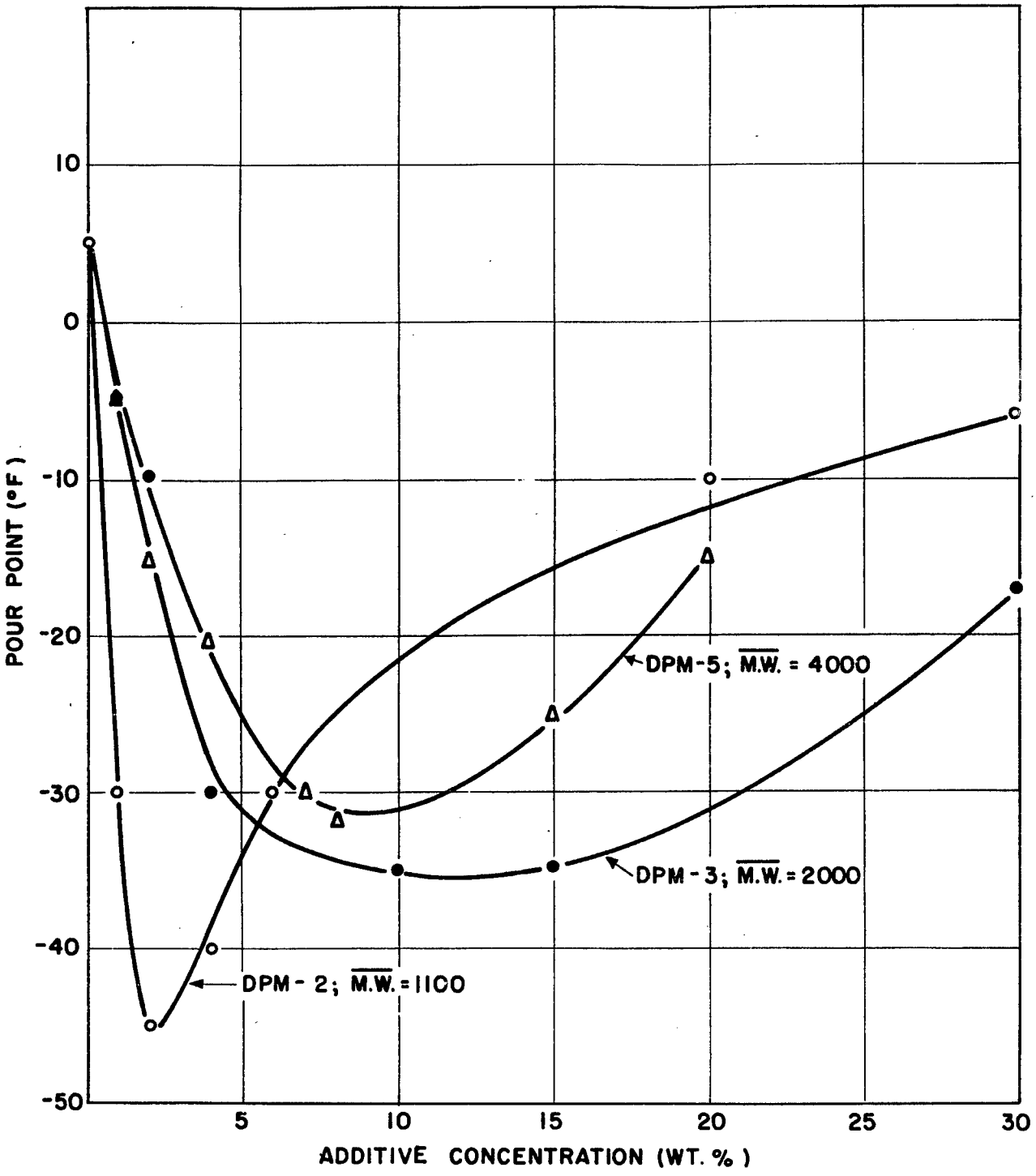


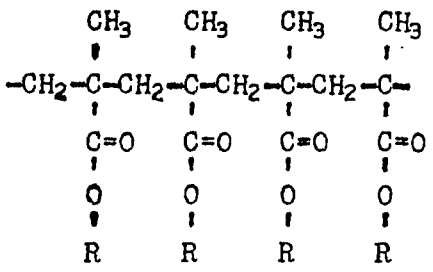
FIG. 7 - PENNSYLVANIA MINERAL SEAL OIL ADDITIVE ACTIVITY OF DODECYL POLYMETHACRYLATE AS A FUNCTION OF AVERAGE MOLECULAR WEIGHT

point depression is a function of the oil as well as the additive. Pour point data for ranges of concentrations of DPM-6, DPM-3, and DPM-2 in Mineral Seal oil are given in Figure 7. Not only is the low molecular weight additive which was relatively inactive in 150 Neutral oil an effective depressant, but it is observed that activity varies inversely with molecular weight.

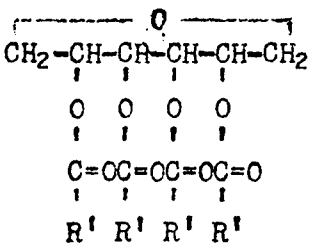
Confirmation of the activity of low molecular weight additives in this oil and their relative inactivity in higher molecular weight 150 Neutral oil was obtained from pour point tests using sorbitol and mannitol tri- and tetradodecanoates as depressants, Table 25. It will be noted from Figure 8 that these materials bear a close structural similarity to the trimer and tetramer of dodecyl methacrylate. Reference to the data shows that they did depress the pour point of Mineral Seal oil but were ineffective in 150 Neutral oil.

Figure 8

TRIMER AND TETRAMER OF DODECYL METHACRYLATE



Tetramer of Dodecyl Methacrylate



Sorbitol or Mannitol Tetradodecanoate

R = n-$C_{12}H_{25}$

R' = n-$C_{11}H_{23}$

Table 25

POUR POINT DEPRESSING ACTIVITY OF SORBITOL AND MANNITOL DODECANOATES

Pennsylvania 150 Neutral Oil

Additive	Additive Conc. (wt. %)	Pour Point (° F)
Mannitol tridodecanoate	4.0	+5
Mannitol tetradodecanoate	4.0	+5
Sorbitol tridodecanoate	4.0	+5
Sorbitol tetradodecanoate	4.0	+5
	Mineral Seal Oil	
Mannitol tridodecanoate	4.0	-25
Mannitol tetradodecanoate	4.0	-25
Sorbitol tridodecanoate	4.0	-10
Sorbitol tetradodecanoate	4.0	-20

4. Effect of Polymer Molecular Weight on Pour Point Depressing Action in Bright Stock

Experiments carried out to determine the susceptibility of Pennsylvania Bright Stock to pour point depression by high, medium and low molecular weight dodecyl polymethacrylate have shown that these materials have no detectable effect on the oil, Table 26. These data corroborate the results obtained with such commercial additives as Acryloid 150, Paraflow PDX, Paraflow 46X and Santopour and is in accord with the idea that the pour point of Bright Stock is not due to wax-oil gelation but to high Newtonian viscosity. Further evidence bearing on this question will be presented in a subsequent discussion of the effect of diluents on physical properties of oils.

B. Acrylic Polymers - Pour Point Depression of Pennsylvania 150 Neutral Oil as a Function of Ester Chain Length

The pronounced pour point depressing qualities of dodecyl polymethacrylate in Pennsylvania 150 Neutral oil have been shown to be associated principally with polymers composed of at least 25 monomeric units. Of equal importance to the dependence of additive activity on polymer chain length is the question of the role of the alkyl group. Roughly the problem was this: Is the dodecyl group present in dodecyl polymethacrylate a unique functional group taking a definite part in the phenomenon of pour point depression or does it simply cause the methacrylate polymer to acquire physical properties the sum of which are essential to the depressant activity?

Table 26

ADDITIVE ACTIVITY OF DODECYL POLYMETHACRYLATE IN PENNSYLVANIA BRIGHT STOCK

Additive Molecular Weight*	Additive Conc. (Wt. %)	Pour Point (° F)
3770	1.0	+10
"	2.0	+10
"	4.0	+10
"	8.0	+10
"	10.0	+10
2340	1.0	+10
"	2.0	+10
"	4.0	+10
"	8.0	+10
"	10.0	+10
"	20.0	+10
"	40.0	+5
860	1.0	+10
"	2.0	+10
"	4.0	+10
"	8.0	+10
"	10.0	+10
"	20.0	+10
"	40.0	+10
"	60.0	+10
"	80.0	0

Cryoscopic

Initially, the investigation involved the preparation and testing of a series of alkyl polymethacrylates ranging from the octyl to the octadecyl esters. Presumably, if the dodecyl group is a specific constitutive factor, other members of the series will not display depressant activity, whereas if its donation to the physical properties of the polymer are its essential value, a pattern of depressant activity proportionate to the variations of the physical property among the group will be evident in a gradation of depressant activity.

In a second phase of experimentation, a series of alkyl polyacrylates were prepared corresponding in alkyl chain length to the polymethacrylates previously tested. A comparison of respective members of the two series provided an additional basis for evaluating the role of the alkyl side chain. The relationship is exemplified by the work of Rehburg and Fisher[10], Figure 9. The brittle points plotted are the temperatures at which standard polymer specimens break with a sudden application of load. Brittle point is closely related to softening point as a measure of polymer crystallinity. It is clear that variation of over-all physical properties with ester chain length is different for the two series. Thus, if the dodecyl group is a constitutive factor it will impart the same properties to either the polymethacrylate or the polyacrylate. Whereas, if the over-all physical properties are the prime consideration in determining additive activity, the variations in activity noted for each series should bear no direct inter-relationship of this sort, but should be dependent upon variations in physical properties.

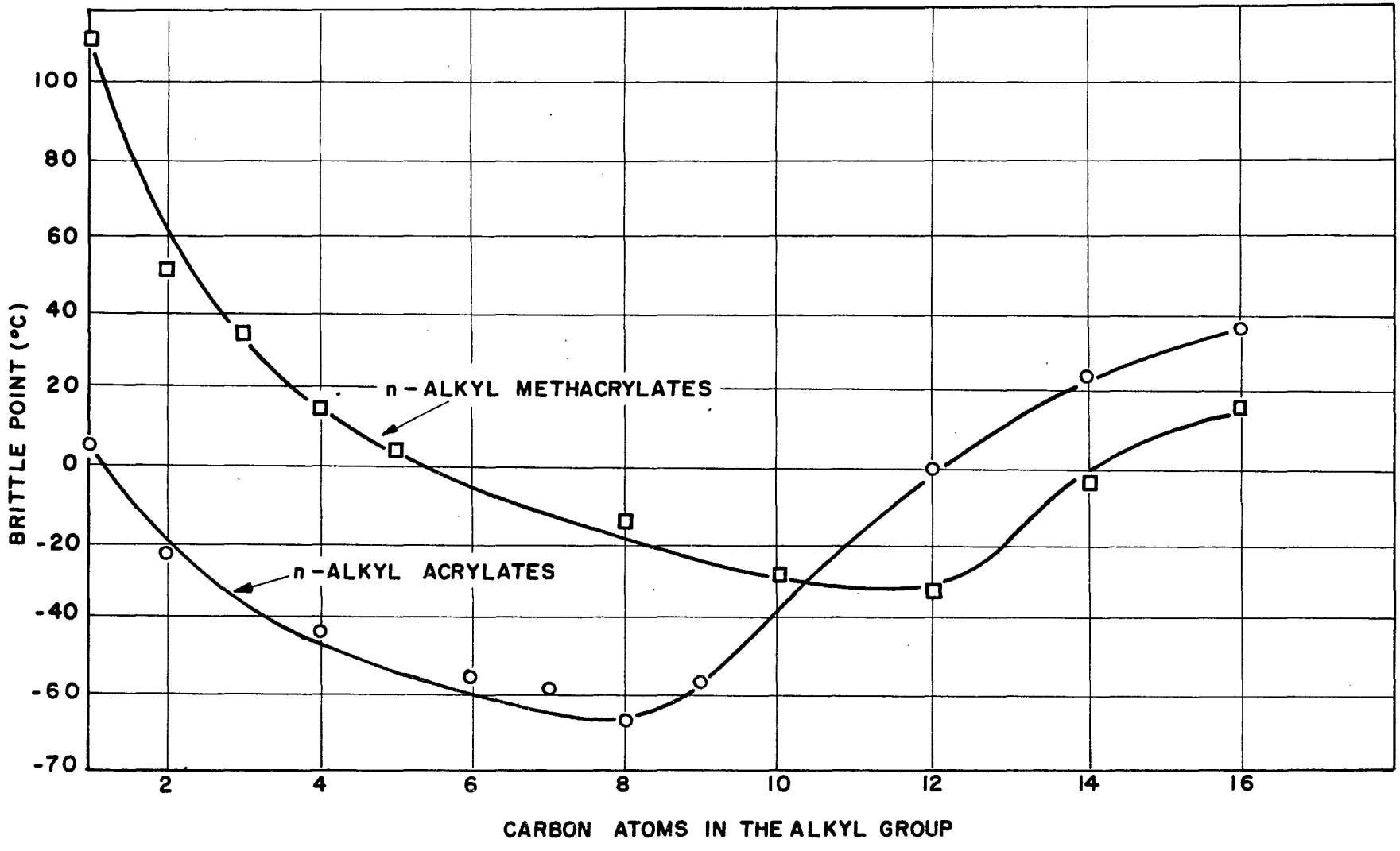


FIG. 9 -BRITTLE POINTS OF POLYMERIC n-ALKYL ACRYLATES AND METHACRYLATES.
REHBURG AND FISHER, IND. ENG. CHEM . 40 . 1429, (1943)

Monomeric octyl, decyl, undecyl, dodecyl, tetradecyl, hexadecyl, and octadecyl methacrylate and octyl, decyl, dodecyl, tetradecyl, and hexadecyl acrylate were obtained from commercial sources or by ester interchange reactions between methyl methacrylate and the appropriate alcohol, according to the procedure of Barrett and Strain[11]. They were polymerized under the reaction conditions used to prepare DPM-6 and DPM-5 for use with Pennsylvania 150 Neutral oil and DPM-2 for use with Mineral Seal oil. Accordingly, the numeral in the code number listed in Table 27 refers to the method of polymerization. Thus, ODPM-5 is octadecyl polymethacrylate polymerized in carbon tetrachloride solution in a solvent to monomer ratio of 20 to 1, corresponding to the method used to obtain DPM-5.

The results of pour point tests are given in Table 27. In comparing the properties of the series of polymethacrylates, the marked feature of the investigation is the inability of polymers having ester chain lengths shorter than 12 carbon atoms to depress the pour points of the oils tested. The variation in activity of polymers having ester chain lengths greater than 12 carbons might be explained on the basis of solubility. However, the lack in continuity of pour point depressing activity of the n-alkyl methacrylate series suggests that this activity is not entirely a function of any over-all property such as solubility that would be expected to vary uniformly through the series, but that the presence of the dodecyl group or longer ester chains is critical.

As a matter of secondary significance, TPM-5 and TPM-6 were equally active in depressing the pour point of 150 Neutral oil. This was not true for the corresponding dodecyl polymethacrylates. Moreover, TPM-5

Table 27

EFFECT OF ESTER CHAIN LENGTH ON POUR POINT DEPRESSING ACTIVITIES OF POLYACRYLATES AND POLYMETHACRYLATES

In Pennsylvania 150 Neutral Oil

Additive	Code No.	Additive Conc. (Wt.%)	Pour Point (° F)
Octyl polymethacrylate	OPM-5	4.0	+5
Decyl polymethacrylate	DEPM-5	4.0	+5
Decyl polymethacrylate	DEPM-5	1.0	+0
Undecyl polymethacrylate	UPM-5	4.0	+10
Undecyl polymethacrylate	UPM-5	1.0	+5
Tetradecyl polymethacrylate	TPM-5	4.0	-20
Tetradecyl polymethacrylate	TPM-5	1.0	-40
Hexadecyl polymethacrylate	HPM-5	4.0	-10
Hexadecyl polymethacrylate	HPM-5	1.0	-5
Octadecyl polymethacrylate	ODPM-5	4.0	-5
Octadecyl polymethacrylate	ODPM-5	2.0	+5
Octadecyl polymethacrylate	ODPM-5	0.5	+5
Octyl polyacrylate	OPA-5	4.0	0
Octyl polyacrylate	OPA-5	1.0	0
Decyl polyacrylate	DEPA-5	4.0	+10
Decyl polyacrylate	DEPA-5	1.0	+10
Tetradecyl polyacrylate	TPA-5	4.0	+30
Tetradecyl polyacrylate	TPA-5	1.0	+15
Hexadecyl polyacrylate	HPA-5	4.0	+45
Hexadecyl polyacrylate	HPA-5	1.0	+5
Decyl polymethacrylate	DEPM-6	4.0	+10
Decyl polymethacrylate	DEPM-6	1.0	+10
Undecyl polymethacrylate	UPM-6	4.0	+10
Undecyl polymethacrylate	UPM-6	1.0	+5
Tetradecyl polymethacrylate	TPM-6	4.0	-25
Tetradecyl polymethacrylate	TPM-6	1.0	-35
Hexadecyl polymethacrylate	HPM-6	4.0	+15
Hexadecyl polymethacrylate	HPM-6	1.0	+5
Octyl polyacrylate	OPA-6	4.0	0

Table 27 (Continued)

EFFECT OF ESTER CHAIN LENGTH ON POUR POINT DEPRESSING ACTIVITIES OF POLYACRYLATES AND POLYMETHACRYLATES

Additive	Code No.	Additive Conc. (Wt. %)	Pour Point (° F)
In Pennsylvania 150 Neutral Oil			
Octyl polyacrylate	OPA-6	1.0	0
Decyl polyacrylate	DEPA-6	2.0	+10
Dodecyl polyacrylate	DPA-6	0.5	-20
Tetradecyl polyacrylate	TPA-6	4.0	+30
Tetradecyl polyacrylate	TPA-6	1.0	+15
Hexadecyl polyacrylate	HPA-6	4.0	+55
Hexadecyl polyacrylate	HPA-6	1.0	+20
In Pennsylvania Mineral Seal Oil			
Octyl polyacrylate	OPA-6	2.0	+5
Octyl polymethacrylate	OPM-5	2.0	0
Decyl polymethacrylate	DEPM-2	2.0	0
Undecyl polymethacrylate	UPM-2	2.0	0
Tetradecyl polymethacrylate	TPM-2	2.0	-5
Hexadecyl polymethacrylate	HPM-2	2.0	-10
Octyl polyacrylate	OPA-2	2.0	0
Decyl polyacrylate	DEPA-2	2.0	0
Tetradecyl polyacrylate	TPA-2	2.0	+10
Hexadecyl polyacrylate	HPA-2	2.0	+20

showed greater activity in a one per cent concentration than in a four per cent concentration.

Solutions in Mineral Seal oil show changes which are too slight to provide a basis for conclusions.

That the presence of the dodecyl group or a longer ester chain is essential to pour point depressant activity of acrylic polymers under the conditions tested is supported by the study of n-alkyl polyacrylates. Reference to Table 27 shows that only dodecyl and longer alkyl chains polyacrylates are depressants in Pennsylvania 150 Neutral oil. However, a 12 carbon side chain alone does not insure depressant activity. In addition, the polymer must possess suitable over-all physical properties such as solubility.

V. DILUENT EFFECT ON THE POUR POINTS OF PENNSYLVANIA STRAIGHT RUN OILS

It has been noted from experiments with dodecyl polymethacrylate and other work based on the use of commercial additives that Pennsylvania 150 Neutral oil can be lowered to a minimum pour of -50° F but cannot be depressed below that value. Two experiments were carried out which indicated -50° F to be at or near the limit attainable by the use of pour point depressants alone.

First, it was found that addition of dodecyl polymethacrylate to Pennsylvania 150 Neutral oils dewaxed to pour points of 5 and -30° F resulted in depression to the same pour point, -50° F. Second, it was observed that dilution of the oil with up to 10 per cent isooctane would not, in itself, depress the pour point of the oil but in the presence of

dodecyl polymethacrylate would effect pour points well below the -50° F limit, Table 28.

It is generally agreed that the congealing of a wax-bearing oil such as Pennsylvania 150 Neutral is due to precipitation of the wax and subsequent gelation of the wax-oil system. Lowering of the pour point by an additive is a result of the modification of this system in such a way as to prevent gelation. Since dewaxing Pennsylvania 150 Neutral oil does not change the minimum pour point attainable with an additive, presumably the effect of the additive is limited to wax-oil gels.

The marked effect of isooctane on the additive treated oil suggests that the -50° F value is a function of Newtonian viscosity, i.e., at -50° F the undiluted oil is too viscous to flow.

For the purposes of the subsequent discussion, the following distinction is made between viscosity pour point and wax or gel pour point. Gel pour point is that temperature below which a non-Newtonian oil will not flow as a result of the formation of a wax-oil gel imparting a yield value to the oil. Viscosity pour point is that temperature below which a Newtonian oil will not flow during the period of the pour point experiment as a result of the low fluidity of the oil. "Fluidity" which is the reciprocal of viscosity will be used hereafter since the fluidity of a solution is approximately an additive function of the fluidities of the individual components on a molar basis.

A. Survey of Diluent Effect on Pennsylvania 150 Neutral Oil

Pour point data obtained for solutions of a variety of diluents in Pennsylvania 150 Neutral oil in the presence and absence of dodecyl

Table 28

THE EFFECT OF A DILUENT ON THE POUR POINT OF 150 NEUTRAL OIL WITH AND WITHOUT A POUR POINT DEPRESSANT

Concentration of Isooctane (wt. %)	Concentration of Pour Point Depressant (wt. %)	Pour Point (°F)
0	0	+5
10	0	+5
0	4	-50
10	4	<-70

polymethacrylate are presented in Table 29. No structural effects were noted except insofar as structure determined the diluent fluidity. If the freezing or pour point of the diluent was below -50° F, the diluent, irrespective of the structure, ordinarily depressed the pour points of four per cent solution of dodecyl polymethacrylate in 150 Neutral oil below the -50° F limit. Di-(2-ethylhexyl) sebacate offered the single exception; however, its pour point is so close to -50° F that its fluidity at that temperature is too close to that of the oil to exert an effect. In no instance did a diluent in concentrations of ten per cent or less depress the pour point of oil containing no depressant.

It is suggested from the data obtained that the only function of the diluents in depressing the pour point of a Pennsylvania 150 Neutral oil solution of dodecyl polymethacrylate below -50° F is to increase the fluidity of the blend at that temperature. Conversely, the occurrence of a viscosity pour point is the most likely action limiting the effectiveness of a pour point depressant in that oil.

B. Variation in Isooctane Effect on the Pour Points of Pennsylvania Straight Run Oil Fractions

Data describing the action of isooctane on Mineral Seal oil, 150 Neutral oil and Bright Stock are being presented here to provide a consistent basis for understanding the effect of diluents. The variations among the susceptibilities of various oil fractions to pour point depression by diluents emphasize the factors contributing to the pour point characteristics of each oil.

Table 29

POUR POINTS OF PENNSYLVANIA 150 NEUTRAL OIL--DILUENT BLENDS

Diluent	Diluent Conc. (wt. % of total blend)	Additive* Conc. (wt. % of oil plus add.)	Pour Point (° F)	Diluent Freezing Point (° F)
None	-	0	+10	
2,2,4-Trimethyl-pentane(isooctane)	2.0	0	+10	-111.3
	4.0	0	+10	
	6.0	0	+5	
	8.0	0	0	
	10.0	0	+5	
	2.0	4.0	-50	
	4.0	4.0	-55	
	6.0	4.0	-65	
	8.0	4.0	-65	
	10.0	4.0	<-70	
n-Octane	2.0	0	+5	-70
	6.0	0	+5	
	10.0	0	+5	
	2.0	4.0	-60	
	6.0	4.0	-65	
	10.0	4.0	-60	
Benzene	2.0	0	+10	+41.9
	6.0	0	+5	
	10.0	0	+5	
	2.0	4.0	-50	
	6.0	4.0	-45	
	10.0	4.0	-45	
Secondary butyl benzene	2.0	0	+10	-117.4
	6.0	0	+10	
	10.0	0	+5	
	2.0	4.0	-50	
	6.0	4.0	-55	
	10.0	4.0	-60	
Di-(2-ethylhexyl) sebacate (Octoil-S)	2.0	0	+10	-69*
	6.0	0	+10	
	10.0	0	+10	
	2.0	4.0	-50	
	6.0	4.0	-50	
	10.0	4.0	-50	
Dewaxed Pennsylvania 150 Neutral Oil	4.0	0	+10	-30**
	8.0	0	+5	
	4.0	4.0	-45	
	8.0	4.0	-45	
	100.0	4.0	-50	

* Dodecyl polymethacrylate, cryoscopic $\overline{MW}$ 4000

** Pour point

Table 29 (Continued)

POUR POINTS OF PENNSYLVANIA 150 NEUTRAL OIL--DILUENT BLENDS

Diluent	Diluent Conc. (wt. % of total blend)	Additive* Conc. (wt. % of oil plus add.)	Pour Point (°F)	Diluent Freezing Point (° F)
Dodecyl polymeth-acrylate ($\overline{MW}$ 860)	2.0	0	+5	+10**
	4.0	0	-5	
	20.0	0	-25	
	40.0	0	-30	
	4.0	4.0	-40	
	6.0	4.0	-40	
	8.0	4.0	-40	
	10.0	4.0	-40	
	20.0	4.0	-30	
	30.0	4.0	-25	
Methylcyclohexane	10.0	0	0	-195.9
	2.0	4.0	-55	
	6.0	4.0	-60	
	10.0	4.0	-70	
Cyclohexene	10.0	0	+5	-154.4
	2.0	4.0	-55	
	6.0	4.0	-60	
	10.0	4.0	-70	
2-Heptene	10.0	0	+5	-100
	2.0	4.0	-50	
	6.0	4.0	-55	
	10.0	4.0	-60	
2-Octene	10.0	0	+5	-100
	2.0	4.0	-55	
	6.0	4.0	-60	
	10.0	4.0	-70	
Isopentane	10.0	0	0	-256
	2.0	4.0	-65	
	6.0	4.0	-70	
	10.0	4.0	-70	
n-Propyl Ether	10.0	0	+5	-187.6
	2.0	4.0	-55	
	6.0	4.0	-65	
	10.0	4.0	-65	
Toluene	10.0	0	+5	-139.6
	2.0	4.0	-50	
	6.0	4.0	-55	
	10.0	4.0	-55	

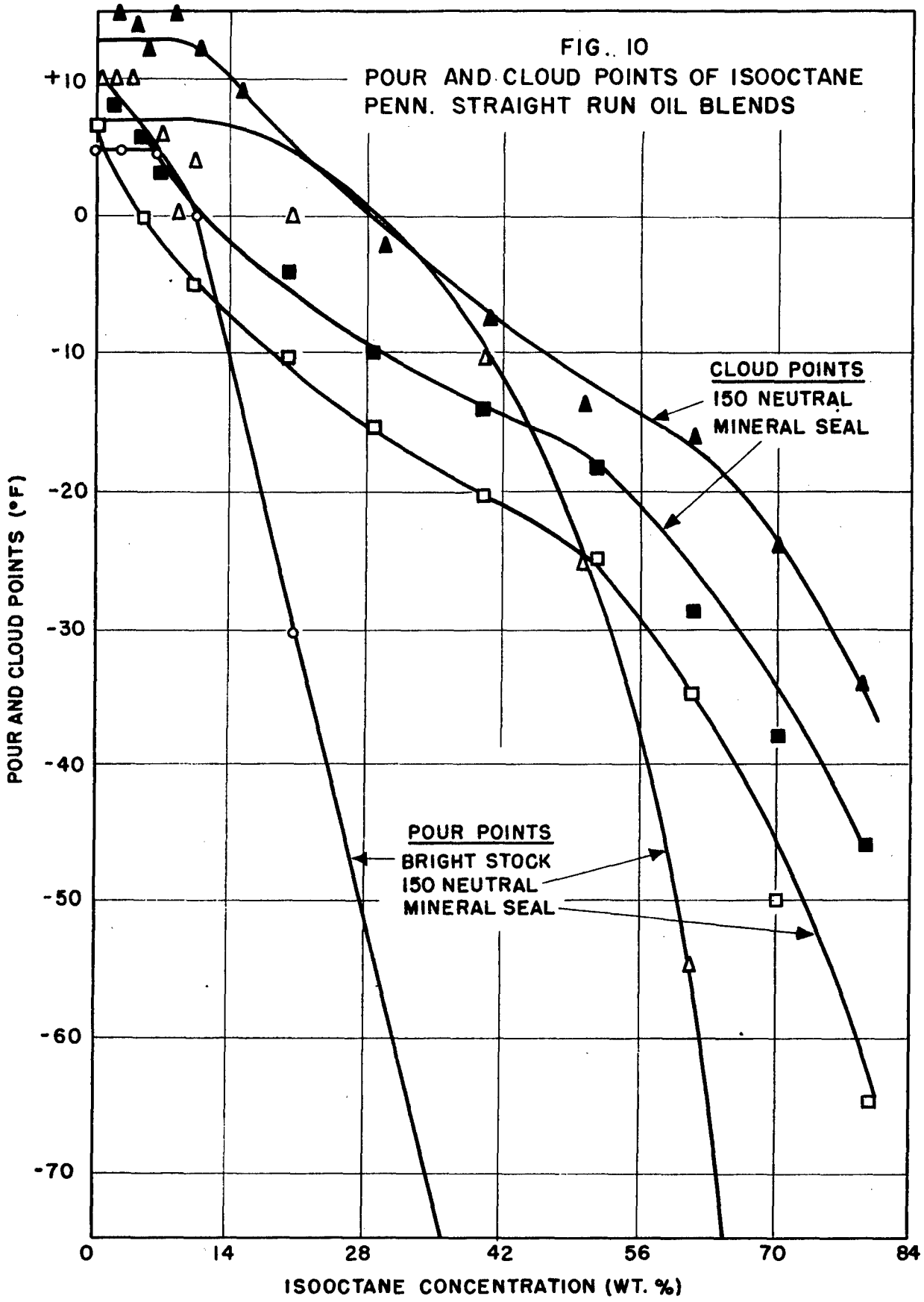
* Dodecyl polymethacrylate, cryoscopic $\overline{MW}$ 4000
** Pour point

1. Isooctane Effect in the Absence of Depressants

Figure 10 presents curves for pour and cloud point data as a function of isooctane concentration in three Pennsylvania straight run oil fractions, Mineral Seal, 150 Neutral and Bright Stock. Before dilution each oil was dewaxed to the same pour point, 5° F.

All observations may be correlated by assuming the independent occurrence of gel and viscosity pour points, the former being caused primarily by wax precipitation and the latter by an intrinsically high Newtonian viscosity. In accordance with this picture each pour point obtained represents the sum of the contributions from each of these two effects. Lamb and Murphy[12] who have reported the effectiveness of low freezing diesters of such acids as adipic and sebacic as diluents in lowering the pour points of natural and synthetic lubricants, have proposed similar ideas. They attribute the relative ineffectiveness of the diesters in high wax content oils to their inability to prevent wax crystallization. The activity of the diluents in low wax content oils is attributed to their effectiveness in increasing the fluidity of the blend.

It is noted that isooctane effects no change on the pour points of 150 Neutral and Bright Stock in the 0-10 per cent and 0-7 per cent concentration ranges, respectively. This is assumed to indicate that the effect of the diluent on wax crystallization and consequently on the tendency of the oil to gel is negligible. The immediate effect of low concentrations of diluent in reducing the pour point of Mineral Seal oil can be ascribed, in the same manner, to an increase in wax solubility.


FIG. 10
POUR AND CLOUD POINTS OF ISOOCTANE
PENN. STRAIGHT RUN OIL BLENDS
+10
0
-10
-20
-30
-40
-50
-60
-70
POUR AND CLOUD POINTS (°F)
CLOUD POINTS
150 NEUTRAL
MINERAL SEAL
POUR POINTS
BRIGHT STOCK
150 NEUTRAL
MINERAL SEAL
0
14
28
42
56
70
84
ISOOCTANE CONCENTRATION (WT. %)

This fact is borne out by the corresponding reduction in cloud point which is a direct measure of wax solubility. Comparison of the lengths of those portions of the curves having zero slope can be taken as an indication that gel formation makes a smaller contribution in Bright Stock than in 150 Neutral oil.

Attention to the right hand portions of the pour point curves will further show the relative importance of gel and viscosity pour point formation on the physical behavior of the three oil fractions. The effectiveness of isooctane as a pour point depressant is clearly greatest for Bright Stock and least for Mineral Seal. If the effect of the diluent were on fluidity alone, this order should be reversed since Mineral Seal is the lighter oil. The most adequate explanation is that the effect of gel structure in determining the pour point is greatest for Mineral Seal and least for Bright Stock. A comparison of the cloud and pour point curves for Mineral Seal oil supports this conclusion. The close proximity of the cloud point curve, which is a plot of the temperature at which the wax begins to crystallize, to the pour point curve indicates that there is an association between wax crystallization and pour point.

It is true that these conclusions have been drawn without detailed phase diagrams of the hydrocarbons involved. However, the effects noted are so gross it is believed that subject to minor corrections they are valid.

As a final suggestion, it may be possible, by the expansion of this study of the relationship between cloud point and pour point for a variety of oils and diluents, to develop a semi-quantitative means for the determination of the relative contributions of gel structure and Newtonian viscosity to the low temperature properties of any oil.

2. Isooctane Effect in the Presence of Dodecyl Polymethacrylate

The action of isooctane on the pour point of additive treated oil was examined more extensively than those of the other diluents mentioned to provide a more detailed example of the results obtainable with a highly fluid material.

Data plotted in Figure 11 illustrate the relationship between polymer concentrations and the pour points of Pennsylvania 150 Neutral oil solutions alone and in blends containing ten per cent isooctane. It is noted that isooctane modifies markedly the relatively flat portion of the curve occurring at approximately -50° F for concentrations of additive in 150 Neutral oil in the one to ten per cent range and facilitates depression to a minimum of approximately -70° F at a two per cent DPM-6 concentration.

Table 29 contains the results of experiments carried out to determine the effects of variations in isooctane concentration on the pour point of a four per cent solution of dodecyl polymethacrylate in Pennsylvania 150 Neutral oil. These data are limited in that pour points lower than -70° F could not be determined in the apparatus used but indicate that the diluent effect is a direct function of concentration.

Concentrations of six, ten and twenty per cent isooctane in untreated Bright Stock are shown in Table 30 to cause pour points of 5, 0 and -30° F, respectively. The addition of four per cent dodecyl polymethacrylate to each of those solutions resulted in a maximum additional depression of 10° F. The relative ineffectiveness of the additive in this regard offers further support for the idea that gel pour point formation is a minor consideration in Bright Stock.

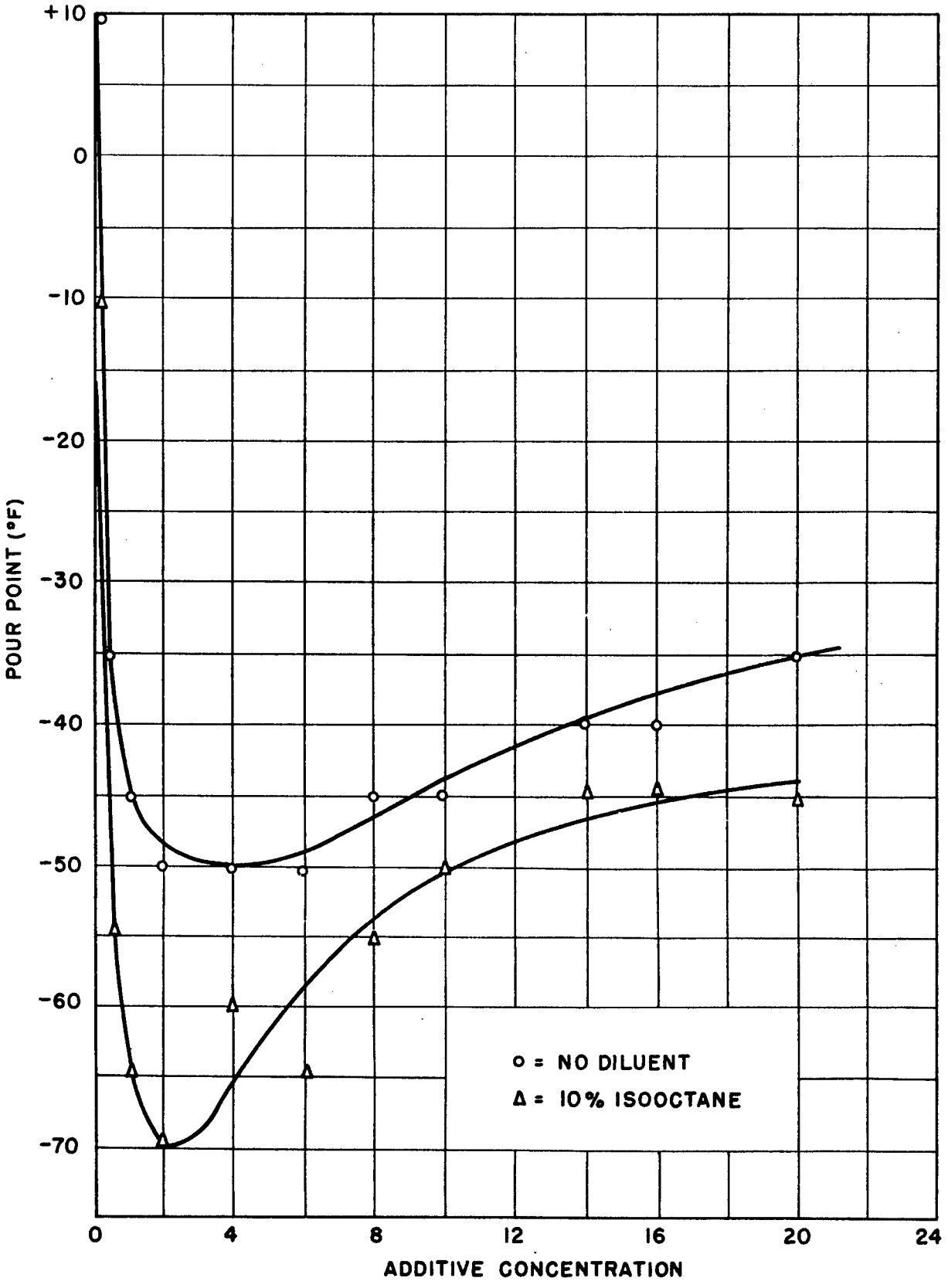


FIG. 11 - POUR POINT DEPRESSING EFFECT OF DODECYL POLY-METHACRYLATE (M.W.=14,000) ON PENNSYLVANIA 150 NEUTRAL OIL WITH AND WITHOUT ISOOCTANE

Table 30

EFFECT OF DODECYL POLYMETHACRYLATE ON PENNSYLVANIA BRIGHT STOCK-ISOOCTANE BLENDS

Isooctane Concentration (wt. % of total blend)	Additive Concentration (wt.% of oil + add.)	Pour Point (° F)
6	0	+5
10	0	0
20	0	-30
6	4.0	0
10	4.0	-10
20	4.0	-40

The tendency of Bright Stock to neutralize the pour point depressing ability of dodecyl polymethacrylate in 150 Neutral oil is illustrated in Table 31. As little as 25 per cent Bright Stock completely negates the action of the additive. It has previously been shown that the relationship between additive physical properties and oil physical properties is critical to the phenomena of pour point depression. Presumably the addition of Bright Stock upset the relationship existing between the 150 Neutral oil and DPM-6.

C. Conclusions

Study of the combined effects of diluents and pour point depressants on mineral oils have shown that the pour point depressants act only to prevent wax-oil gelation. In the presence of an active pour point depressant the pour point of the oil is limited by its viscosity-temperature characteristics. The only materials affecting the pour point further are those affecting these characteristics, i.e., diluents. In the case of the Pennsylvania 150 Neutral oil the minimum pour point attainable with a depressant appears to be -50° F. Since that pour point is attained with commercial materials, it would not be possible to synthesize a depressant more effective on that oil. On the other hand, since gel formation is a relatively unimportant factor in the pour properties of Bright Stock, depression of its pour point must be confined to the use of diluents.

The problem of producing an aviation oil with a viscosity at the working temperature of aircraft engines high enough to provide lubrication and a pour point sufficiently low to facilitate starting engines at arctic temperatures involves two apparently conflicting properties. The oil viscosity

Table 31

POUR POINTS AND VISCOSITIES OF PENNSYLVANIA BRIGHT STOCK-150 NEUTRAL OIL BLENDS

Bright Stock Conc. (wt. % of total oil)	Additive Conc.* (wt. % of total (blend)	Pour Point (°F)	Viscosity				Viscosity Index
			100°F		210°F		
			Centistokes	SUS	Centistokes	SUS	
0	0	+10	-	-	-	-	-
5	0	+10	36.4	169.5	5.61	44.6	100.5
10	0	+10	41.6	192.9	6.15	46.3	102.5
25	0	+10	59.9	277	7.92	52.1	106.5
50	0	+5	113.8	526	12.23	67.2	105.5
75	0	+5	229.4	1060	19.34	95.4	102.6
90	0	+10	404.9	1871	25.8	123.3	102.0
95	0	+5	356.0	1645	28.2	133.9	102.0
100	0	+10	-	-	-	-	-
0	4.0	-50	-	-	-	-	-
5	4.0	-35	60.2	278	9.22	56.5	130.5
10	4.0	-20	66.5	307	9.93	59.0	130.0
25	4.0	+10	93.4	432	12.42	67.9	125.5
50	4.0	+5	171.9	794	18.51	91.9	119.4
75	4.0	+10	323.8	1496	28.6	134.7	117.0
90	4.0	+10	482.7	2230	37.0	172.2	114.0
95	4.0	+10	532.0	2458	37.4	175.2	110.4
100	4.0	+10	-	-	-	-	-

* Dodecyl polymethacrylate MW 4000 - Cryoscopic

at high temperatures must be high enough for lubrication and at low temperatures low enough to display a low viscosity pour point in the presence of depressants. In the light of the information, the most likely solution other than dilution appears to be the development of a very high viscosity index oil. An example of the possibilities may be found in the use of high concentrations of high molecular weight dodecyl polymethacrylate as both a viscosity index improver and a pour point depressant in Pennsylvania 150 Neutral oil. Table 24 shows that a viscosity range of 150-3200 SUS/100° F and a pour point range of -35° F to -50° F may be attained with the use of the polymer having an average molecular weight of 14,000.

VI. POUR POINT DEPRESSION OF BLENDS OF PURE n-PARAFFINS IN DEWAXED PENNSYLVANIA 150 NEUTRAL OIL

Studies of the action of pour point depressants on the natural waxes precipitated from mineral oil is complicated by the large number of chemical components making up the wax. Composition and physical properties such as crystal habit and crystal structure as well as changes in these properties are indeterminate.

To provide a well-defined system in which changes resulting from the action of pour point depressants could readily be recognized, natural waxes were removed from Pennsylvania 150 Neutral oil by dewaxing at -60° F (see Appendix B) and replaced with pure synthetic normal paraffin hydrocarbons having molecular weights and melting points in the range of the extracted material. The paraffins used comprised the series n-eicosane to

It is not suggested that the synthetic blends duplicate the complex conditions present in mineral oils. However, preliminary experiments disclosed that any desired pour point could be produced with the paraffins. Moreover, polymethacrylates previously found to be depressants in Pennsylvania 150 Neutral oil were also depressants for the synthetic systems.

A. Pour Properties of Synthetic Blends

Figure 12 shows the dependence of pour point on wax concentration for systems containing single wax components. Plots of pour points as the reciprocal of the absolute temperature against the logarithms of the wax concentrations are straight lines typical of solubility relationships. This lends credence to the association between wax crystallization temperatures and pour points. Cloud points follow the same curves at temperatures 0-6° F higher.

Pour points were measured by a micro method developed to permit a large number of determinations with a minimum quantity of pure paraffins, Appendix B. Engel and Wahlberg[13] have pointed out that pour points due to wax-oil gelation are independent of sample size. Observations made in the present work are in agreement. Wax pour points of Pennsylvania 150 Neutral oil as determined by ASTM procedure were duplicated with the micro technique. In addition, in the experiments to be subsequently described, determinations of the pour points of several samples with equal concentrations of the same paraffin wax gave reproducible results.

As may be expected for systems containing more than one paraffin, the gelation effect is colligative if the components can form a solid solution. If they cannot, the pour point observed corresponds to that produced

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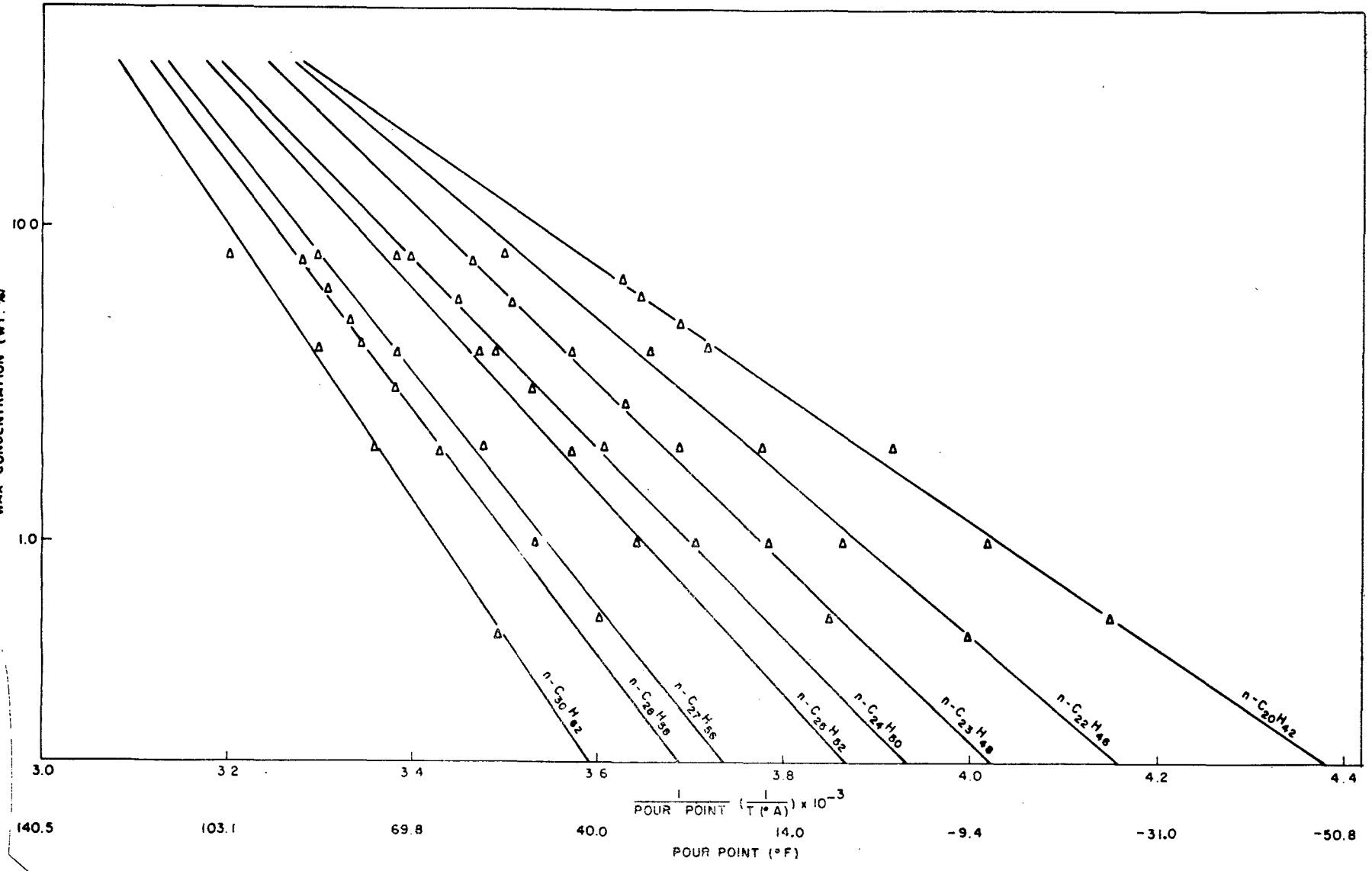


FIG. 12 - POUR POINTS OF NORMAL PARAFFIN - DEWAXED PENNSYLVANIA 150 NEUTRAL OIL BLENDS

by the wax precipitating first. This is shown in Table 32.

B. Habits of Pure n-Paraffins Crystallized from Synthetic Blends

The habits of the pure waxes crystallized from eight per cent solutions in the dewaxed oil are illustrated in Figure 13 and presented more completely in Appendix C. The preparations of the sample slides are described in Appendix B. Those samples with cloud points above room temperature were viewed and photographed with a Galileo Universal microscope, while a Spencer microscope fitted with a cold stage, (see Appendix B), and a Kodak Visicam camera was used with those which crystallized below room temperature. Phase contrast illumination was used in all cases to provide optimum field contrast.

With the exception of n-eicosane which crystallized as a web-like network of needles, the waxes all precipitated as plates and blades. Their marked features are thinness and flexibility. A plausible picture of the gel structure may be developed in which resistance to flow results from the formation of an infinite three-dimensional wax system by the interlocking or intergrowth of crystals. The growth of the wax into large thin plates and blades with high surface area:volume ratios results in a high probability for the process.

C. Action of Pour Point Depressants on the Pour Properties of Synthetic Blends

Pour point depression of synthetic n-paraffin wax- dewaxed oil blends with acrylic polymers showed a parallel with results obtained in Pennsylvania 150 Neutral oil bearing natural wax. Dodecyl, tetradecyl and hexadecyl polymethacrylates were depressants in both natural and synthetic

Table 32

MICRO POUR POINT OF NORMAL-PARAFFIN WAX MIXTURES—DEWAXED 150 NEUTRAL OIL BLENDS

Composition of Wax Mixtures						Oil Sample Containing Wax Mixture	
Solute A n-Eicosane (wt. %)	Solute B n-Heneicosane (wt. %)	Solute C n-Octacosane (wt. %)	Oil Sample Containing Single Solute Pour Point (°F)			Cloud Point (°F)	Pour Point (°F)
			A	B	C		
2.04	0.00	2.01	4	-	66	66	66
9.07	0.00	1.81	44	-	62	64	62
2.34	2.29	0.00	8	26	-	34	34



13A n-EICOSANE
(CLOUD POINT 38° F)



13B n-DOCOSANE
(CLOUD POINT 58° F)



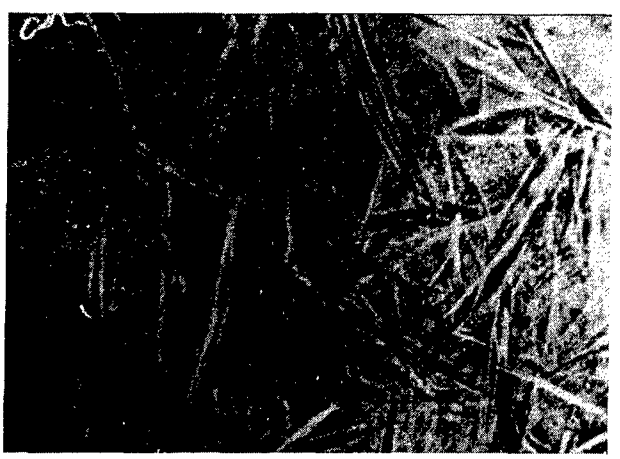
13C n-TETRACOSANE
(CLOUD POINT 72° F)



13D n-PENTACOSANE
(CLOUD POINT 76° F)



13E n-OCTACOSANE
(CLOUD POINT 92° F)



13F n-TRIACONTANE
(CLOUD POINT 106° F)

FIG. 13 - SYNTHETIC n-PARAFFINS (8.00 WT. PER CENT) CRYSTALLIZED FROM DEWAXED PENNSYLVANIA 150 NEUTRAL OIL

MAGNIFICATION 250 X

blends. Octyl, decyl and undecyl polymethacrylates and octyl and decyl polyacrylates which had been ineffective in the original oil were also non-depressants in blends of n-octacosane and n-eicosane with the dewaxed oil. It was found that such commercial depressants as Paraflow, Santopour and Pourex also depressed the pour points of the synthetic blends.

In correlating the effects of the polymers on n-eicosane and n-octacosane blends, the bar-graphs shown in Figure 14 emphasize the relationship between additive and wax concentrations, additive pour point depressing activity, and pour points in the absence of depressants. The data therein presented are termed "pour point depression", "weak pour point depression" and "no pour point depression" because of the limitations of the micro method. As was previously explained, the procedure is satisfactory only for determining wax pour points. Pour point depressants prevent wax-oil gelation and consequently the occurrence of wax pour points. In the absence of strong gelation, a viscosity pour point is observed and it is affected markedly by sample size. Since viscosity pour points are empirical, their values are not noted except qualitatively as follows: Experiments carried out with blends in the absence of depressants had shown that the pour points occurred no more than six degrees below the cloud points. Additives which did not increase that range were considered non-depressants. On the other hand, it was empirically found that additive blends which poured 20 degrees below their cloud points had pour points considerably lower, and that the sample displayed a gradual increase in viscosity in the range of its pour point typical of an approach to a viscosity pour point. As a consequence, these samples were considered to display "pour point depression".

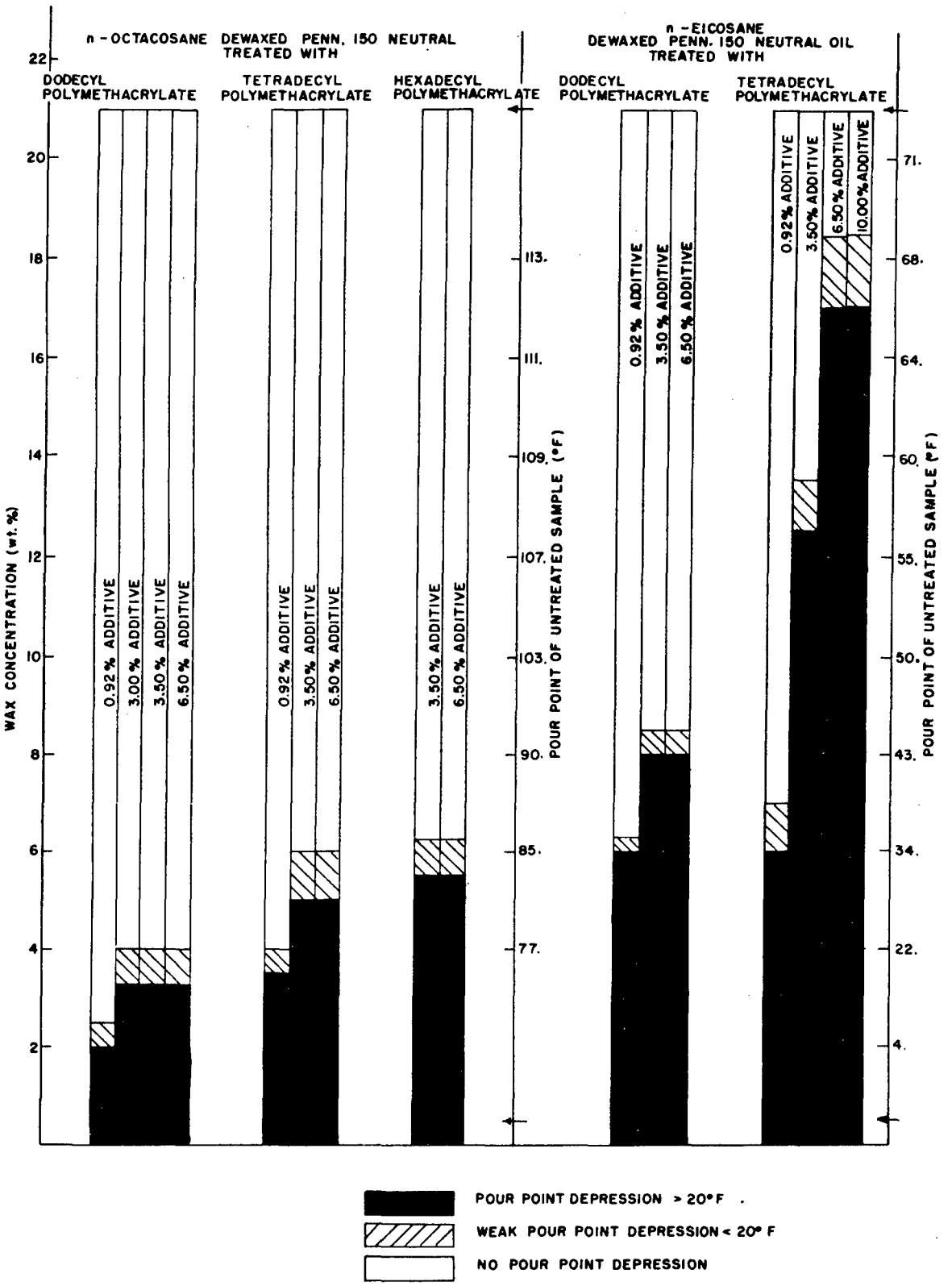


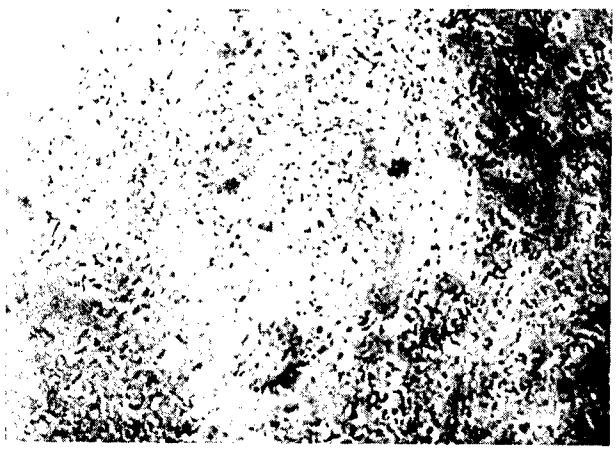
FIG. 14
WAX CONCENTRATION — POUR POINT DEPRESSANT CONCENTRATION RELATIONSHIP
FOR
PURE NORMAL PARAFFIN — DEWAXED OIL BLENDS

Those blends with spans of 6-20 degrees between their cloud and pour points were considered to display "weak pour point depression".

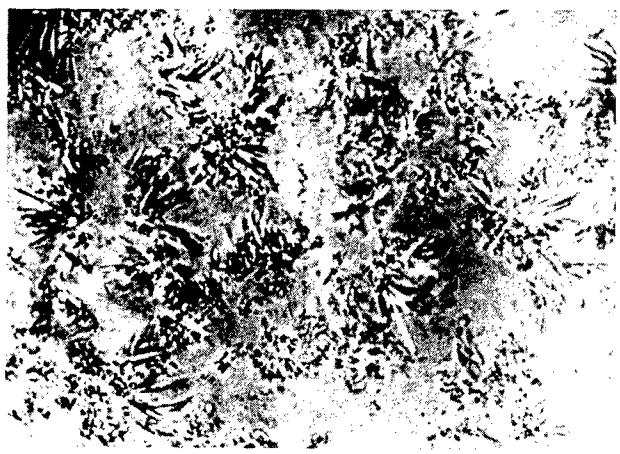
The marked feature of the pour point depressing process is the specification of a limiting value for wax concentration beyond which pour point depression will not occur. In most cases 3.00-3.50 per cent additive depresses the pour point of that maximum wax concentration and increasing the additive to 6.50 per cent does not increase the amount of wax on which the additive is effective. The limiting wax concentration appears to be partially dependent upon the additive structure. For the combination studied polymethacrylate activity increases with ester chain length. Of special interest is the ability of tetradecyl polymethacrylate to depress the pour point of a blend containing as much as 17 per cent n-eicosane.

D. Effect of Pour Point Depressants on the Habits of Pure n-Paraffins Crystallized from Synthetic Blends

Investigation of the crystal habits of pure normal paraffin waxes crystallized out of oil has shown that all instances of pour point depression are accompanied by changes in wax crystal habit. When the pure normal paraffin waxes, the habits of which are illustrated in Figure 13 and shown completely in Appendix C, were crystallized in the presence of hexadecyl polymethacrylates, the crystal habits exemplified in Figure 15 resulted. The entire series of habits appears in Appendix C. The principal characteristic change in the crystals precipitated from additive solution is their decrease in surface area:volume ratios. Their bulkiness is evident in their



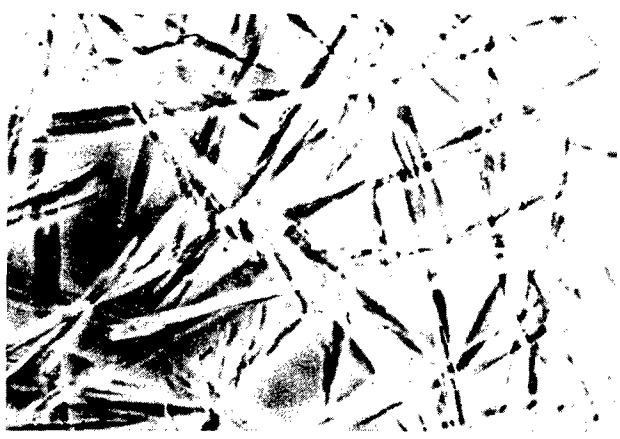
15A n-HENEICOSANE



15B n-DOCOSANE



15C n-TETRACOSANE



15D n-OCTACOSANE

FIG. 15 - SYNTHETIC n-PARAFFINS (8.00 WT. PER CENT) CRYSTALLIZED FROM DEWAXED PENNSYLVANIA 150 NEUTRAL OIL CONTAINING HEXADECYL POLYMETHACRYLATE (3.50 WT. PER CENT)

MAGNIFICATION 250 X

shapes and the increased ease with which they could be distinguished under the microscope. Another item of interest is the increase in crystal size from n-eicosane to n-triacontane.

The dependency of the crystal habit of n-octacosane upon the ester chain length of polymethacrylates is shown in Figures 16 and 17. Those polymers which did not depress the pour points of n-octacosane-dewaxed oil blends did not affect the crystal habit of the precipitated wax, Figure 16, while those which were depressants caused habit changes, Figure 17. In corresponding tests with commercial additives, Figure 17, all instances of depression are accompanied by alterations in wax crystal habit. A complete series of photomicrographs may be found in Appendix C.

The relationship between pour point depressing activity and ability to cause changes in crystal habits for dodecyl, tetradecyl and hexadecyl polymethacrylates is found in a comparison of photomicrographs presented in Figure 17. It is noted that the hexadecyl polymer which had been shown to depress the greatest concentration of n-octacosane produced the greatest change in crystal habit, while the twelve carbon ester exerted the least influence on both the pour and crystal properties of the blend. The magnitude of the alteration in habit is reflected in a progressive increase in the bulkiness of the crystals from thin sheets to irregularly shaped plates and tablets formed in the presence of dodecyl polymethacrylate to long massive needles with the hexadecyl polymer.

Analysis by x-ray diffraction of n-octacosane and n-heptacosane blends with dewaxed oil below their cloud points showed that, despite gross changes in crystal habit due to tetradecyl polymethacrylate, the crystal



16A NO ADDITIVE



16B DECYL POLYMETHACRYLATE



16C UNDECYL POLYMETHACRYLATE



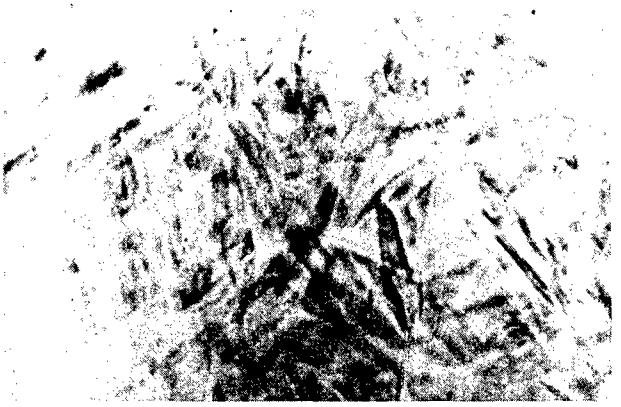
16D DECYL POLYACRYLATE

FIG. 16 - EFFECTS OF NON - POUR POINT DEPRESSING ACRYLIC POLYMERS ON THE HABIT OF n-OCTACOSANE CRYSTALLIZED FROM DEWAXED PENNSYLVANIA 150 NEUTRAL OIL

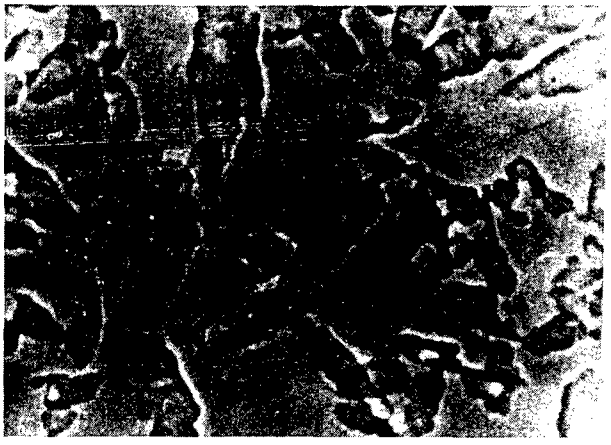
MAGNIFICATION 250 X



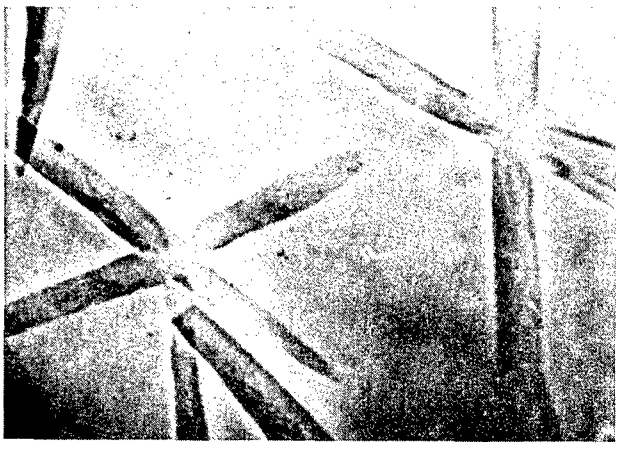
17A NO DEPRESSANT
n-OCTACOSANE (8.00 WT. %)



17B DODECYL POLYMETHACRYLATE
(3.50 WT. %)
n-OCTACOSANE (8.00 WT. %)



17C TETRADECYL POLYMETHACRYLATE
(3.50 WT. %)
n-OCTACOSANE (8.00 WT. %)



17D TETRADECYL POLYMETHACRYLATE
(3.50 WT. %)
n-OCTACOSANE (2.90 WT. %)



17E HEXADECYL POLYMETHACRYLATE
(3.50 WT. %)
n-OCTACOSANE (8.00 WT. %)



17F COMMERCIAL ADDITIVE
(3.50 WT. %)
n-OCTACOSANE (8.00 WT. %)

FIG. 17 - EFFECTS OF POUR POINT DEPRESSANTS ON THE HABIT OF n-OCTACOSANE CRYSTALLIZED FROM DEWAXED PENNSYLVANIA 150 NEUTRAL OIL
MAGNIFICATION 250 X

structure is neither changed basically nor slightly deformed. Reflection intensities for the n-heptacosane blend obtained with the Phillips-Norelco X-Ray Spectrophotometer in conjunction with a Geiger counter are given in Figure 18. Crystal habit changes occurring in the absence of structure changes may be attributed to a surface phenomenon such as adsorption.

E. Conclusions as to the Mechanism of Pour Point Depression

On the basis of the crystallographic and pour characteristics of the blends of synthetic pure normal paraffin hydrocarbons and dewaxed Pennsylvania 150 Neutral oil, a mechanism for the action of pour point depressants may be proposed. The occurrence of a wax pour point is attributed to the ability of the crystallized wax to form a rigid three-dimensional structure by crystal interlocking or intergrowth. In the absence of a pour point depressant the waxes studied crystallize as thin extensive sheets with a high ratio of surface area:volume. This growth process results in a high probability of intercrystalline contact and, irrespective of the mechanism of bonding, fosters gelation by the process suggested.

The action of the additive in lowering the pour point is to produce a wax crystal modification less susceptible to formation of a continuous network. The adsorption of the depressant by crystal faces would inhibit further deposition on those faces causing a change in the relative growth rates of all faces and resulting in an altered habit. In the cases of the pure hydrocarbons, the adsorption of the polymethacrylates by the ordinarily rapidly growing faces is considered to cause the change

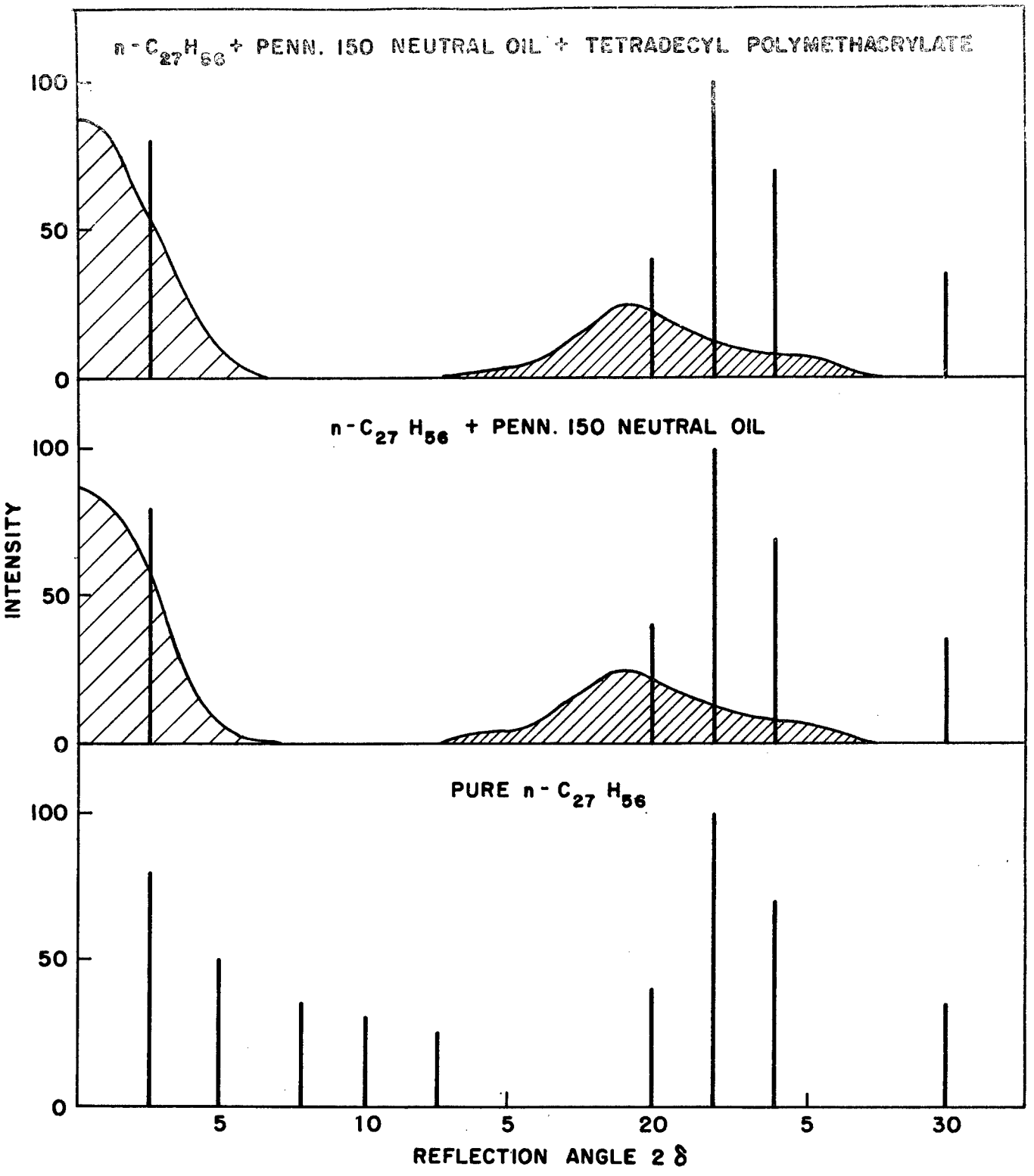


FIG. 18-EFFECT OF POUR POINT DEPRESSANT ON X-RAY DIFFRACTION PATTERNS OF n-HEPTACOSANE

in habit from the large thin plates to bulkier crystals. In addition to causing a habit change to one less susceptible to gelation, the adsorption of the depressant may render the additive coated faces relatively inaccessible to intercrystalline bonding. Thus, the action of the polymethacrylate depressants in being adsorbed by crystal faces of precipitating pure paraffin hydrocarbons may be twofold. First, they decrease the probability of intercrystalline contact thereby producing a habit with a decreased ability to form the continuous wax network. Second, the crystal face bearing the adsorbed additive may be relatively inaccessible to the crystal interlocking or intergrowth causing gelation.

F. Properties of Additives Requisite to Pour Point Depressing Activity

Molecular requirements of pour point depressants as fixed by studies of acrylic polymers appears to be a branched chain structure in which the side chain length is at least twelve carbon atoms. The optimum over-all molecular weight will be determined by the functional groups present in the molecule but in general must be commensurate with suitable over-all physical properties.

For instance, as a rough rule of the thumb it is believed that the polymer must be deposited from oil solution with wax to be effective as a depressant. Thus, the additive molecular weight must be such as to exhibit the proper solubility in the particular oil to be treated.

VII. SYNTHESIS OF POUR POINT DEPRESSANTS - CONDENSATION POLYMERS

Syntheses of new pour point depressants were carried out using the molecular design prescribed in the preceding section. A polyesterification, a reaction of a dibasic acid and a dihydric alcohol, was chosen to provide condensation polymers with well-defined compositions. The experimental procedures are described in Appendix B. The need for an alkyl chain of at least 12 carbon atoms was met with the use of such compounds as 1,2-tetradecanediol and glyceryl monolaurate, while succinic and phthalic anhydrides provided the polymers with aromatic and aliphatic backbones. The following is a list of the materials synthesized. Their structures are illustrated in Figure 19.

poly-1,2-tetradecylene succinate

poly-1,2-hexadecylene succinate

poly-1,2-tetradecylene phthalate

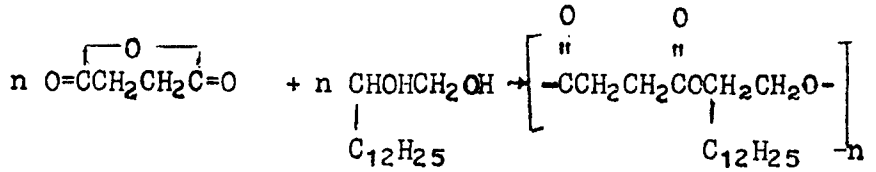
poly-1,2-hexadecylene phthalate

polylauroylglyceryl phthalate

polystearoylglyceryl phthalate

Figure 19

POLY-1,2-TETRADECYLENE SUCCINATE



A critical factor providing requisite physical properties is the molecular weight of the polymer. In the cases of the condensation products,

the problem was the attainment of molecular weights high enough to provide depressant activity. This was accomplished by the use of vigorous conditions for the removal of water, the product of the esterification, from the reaction mixture (Appendix B). Active depressants were, in all cases, soft, rubbery, tacky solids having average molecular weights at least in the range of 3000.

A. Definition of Pour Point Depressing Requirements

The ultimate object of the syntheses was to produce an additive capable of depressing the pour point of a blend of oil formulated to meet specification No. MIL-L-6082A for grade 1100 aviation oil. The two base stocks used were typical blends of Bright Stock and Neutrals sold as 1100 grade aviation lubricants with the exception that they contained no pour point depressant. The pour points of these products determined in our laboratories were 20 and 25° F. Specification No. MIL-L-6082A required that those pour points be reduced to at least 10° F.

B. Pour Point Depression with Condensation Polymers

It had been established that the problem was to synthesize a material capable of depressing the pour point of a blend of Bright Stock and less viscous wax-bearing Neutral oil with a pour point of approximately 20° F. Tests carried out with dodecyl and tetradecyl polymethacrylates in Pennsylvania 150 Neutral oils with pour points of 5 and 30° F and in the 1100 grade aviation oil disclosed that only the depressant capable of effecting the higher pour point Neutral was a depressant in the aviation blend. Dodecyl polymethacrylate was active in the 150 Neutral with a 5° F

pour point but not in either the Neutral with the pour point of 30° F or in the 1100 grade oil. On the other hand, the tetradecyl polymer which was effective in both of the 150 Neutrals depressed the pour point of the aviation oil to -10° F. It was also noted that stearyl polymethacrylate was too insoluble in any of the oils to be a depressant.

This data proved valuable in the preparation of an effective condensation polymer. The dodecyl derivatives, which were the first synthesized, poly-1,2-tetradecylene succinate, poly-1,2-tetradecylene phthalate and polylauroylglyceryl phthalate were all inactive in 1100 grade aviation oils. Likewise, tests carried out with the two Pennsylvania 150 Neutral oils disclosed that those materials were depressants in the low pour point oil but not in the high. This paralleled the activity of dodecyl polymethacrylate. In addition, it was found that polystearoylglyceryl phthalate was not a depressant due to its low solubility in the oils.

In view of the comparison between the activities of the polymethacrylates and the condensation polymers, emphasis was placed on the synthesis of structures corresponding to tetradecyl polymethacrylate. The first such material was a poly-1,2-hexadecylene phthalate. It showed pour point depressing activity in the aviation oil equal to those of commercial depressants and in a range which indicates that optimum depression has been achieved. Pertinent data are presented in the next section.

C. Evaluation of Poly-1,2-hexadecylene Phthalate

The poly-1,2-hexadecylene phthalate found to be effective as a pour point depressant for aviation oil has the typical appearance of a

taffy-like solid with no noticeable tendency to crystallize. It was prepared at 180° C (356° F) and no tendency for the pure material to degrade thermally was noted at that temperature. Other physical properties appear in Table 33.

Table 33

PHYSICAL PROPERTIES OF POLY-1,2-HEXADECYLENE PHTHALATE PREPARED AS POUR POINT DEPRESSANT

Vapor Pressure:	< 1 mm Hg at 180° C (356° F)
Freezing Point:	glass
Flash Point :	> 500° F
Viscosity :	> 2000 SUS/210° F
Density :	approximately 0.9
Average Molecular Weight:	3000
Evaporation :	none
Solubility :	Soluble in chlorinated solvents, benzene, petroleum ether (65-110) slightly soluble in alcohol

The effect of this material on two typical commercial 1100 grade aviation oils is shown in Table 34. The data shows clearly that its activity as a pour point depressant is at least equivalent to that of two well-known commercial materials, Paraflow 46X and Acryloid 150. As may be surmized, the effect of poly-1,2-hexadecylene phthalate on Pennsylvania 1100 grade aviation oil, as shown by the data contained in Table 35, is negligible. The results of corrosion and oxidation stability tests are given in Tables 36 and 37. Rust inhibition was measured by the static water drop test.

Table 34

POUR POINT DEPRESSING PROPERTIES OF POLY-1,2-HEXADECYLENE PHTHALATE

	Pour Points (°F)			
Base Oil	No Additive	Paraflow 46X*	Acryloid 150*	Poly-1,2-Hexadecylene Phthalate*
Sinclair Penn. 1100 Grade Aviation Oil	20	0	-10	-15
Tide Water Penn. 1100 Grade Aviation Oil	25	0	-10	- 5

*All additive concentrations are 1%

1. 0.5 to 0.25% of the polymer in the Sinclair oil yielded pour points of -10 and -5 respectively.

2. Specifications for 1100 grade oil are a pour point of 10°F and a solvent pour point of -65°F.

3. The polymer in a 1% concentration produced a solvent pour point of -75°F in the Sinclair oil.

(Specifications for solvent pour point according to MIL-L-6082A are: Solvent blend 70% oil + 30% diluent-by volume; diluent = 20% xylene + 80% naphtha-by volume)

Table 35

PHYSICAL PROPERTIES OF PENNSYLVANIA 1100 GRADE AVIATION OIL A

COMPOUNDED WITH POLY-1,2-HEXADECYLENE PHTHALATE

	Untreated Oil	Poly-1,2-Hexadecylene Phthalate Treated Oil
Flash Point	480°F	480°F
Fire Point	520°F	520°F
Ash	0.00%	0.00%
Precipitation number	0.00	0.00
Sulfur	0.074%	0.080%
Viscosity 100°F (SUS)	1096.8	1047.4
Viscosity 210°F (SUS)	97.8	96.4
Viscosity index	104	105
Color-Tag Scale	1.3	1.2
Color-NPA Scale	7	7
Conradson Carbon	0.67%	0.64%

Table 36

RESULTS OF THE STATIC WATER DROP TEST

PENNSYLVANIA 1100 GRADE AVIATION OIL-A

	Corrosion Scale Number			
	1 Hour	24 Hours	48 Hours	Observations
Untreated Oil	4-6	5-8	8-8	Black and red corrosion products
Oil Containing Poly-1, 2-hexadecylene Phthalate	1-1	3-7	5-10	Black corrosion products Black annular ring around bubble area

Table 37

OXIDATION TEST DATA

PENNSYLVANIA 1100 GRADE AVIATION OIL

	Untreated Oil	Oil Containing Poly-1, 2-hexadecylene Phthalate
Neutralization Number		
Unoxidized oil	0.038	0.087
Oxidized oil	4.88	3.90
Vol. acids generated(mg.KOH/mg.oil)	2.4	1.5
Viscosity at 100°F (cs.)		
Unoxidized oil	238.9	224.2
Oxidized oil	252.6	274.9
Condition of Metal Catalysts		
Aluminum	no corrosion	no corrosion
Copper	very slight stain	heavily etched
Steel	no corrosion	no corrosion
Color of Oil		
Unoxidized oil	brown-green	brown-green
Oxidized oil	red brown	red-brown

A specially prepared 1020 steel specimen containing a conical depression was immersed in the oil and equilibrated for one hour at 60° C. 0.2 ml of doubly distilled water was added to the depression and the sample was monitored at 1, 24 and 48 hour intervals. The relative density and area of corrosion are indicated by a two digit scale of 10. The first number is the corrosion density and the second number is the area covered by the resultant drop. A figure of "4-6" would be interpreted as a moderately heavy concentration of corrosion products covering 60 per cent of the bubble area.

The oxidation stability of the two blends was determined in the presence of dissimilar metal couples under carefully controlled accelerated conditions of aeration and temperature in an apparatus of the type described in Bureau of Aeronautics Specification 14L16 (Aer). The changes in neutralization number, viscosity and amount of evolved volatile acids were monitored. In addition, the polished steel, copper and aluminum surfaces were checked for evidence of corrosion. The results are summarized in Table 37. There are no significant differences between the two oils on the basis of this test since the fact that the blend containing the pour point depressant etches the copper surface.

VIII. RHEOLOGICAL STUDIES OF LUBRICATING OILS

A. Pennsylvania 150 Neutral Oil Below the Pour Point

1. Studies with the Interchemical Rotational Viscometer

Initial studies on the rheology of wax bearing lubricating oils below the pour point were confined to one oil, a Pennsylvania 150 Neutral oil which had been dewaxed to a pour point of +5° F (-15° C). The non-

Newtonian flow behavior of this oil at -25° and -30° C (-13° and -22° F) as observed with the Interchemical Rotational viscometer has been described in detail in previous reports[14] and is also summarized in a publication[15], which is included in this report as Appendix D. Only the essential points and conclusions of that work, therefore, will be presented here.

In this exploratory experimentation it was found that Pennsylvania 150 Neutral oil below its pour point exhibited two distinctly different types of thixotropy,* superimposed, when studied in the concentric-cylinder rotational viscometer. When subjected to shearing at low shear rates the apparent viscosity of the oil decreased irreversibly as a function of time to a minimum viscosity. At high shear rates this irreversible decrease becomes too rapid to be observed experimentally, however, another thixotropic effect which is reversible becomes pronounced.

The former effect, i.e., the thixotropy at low rates of shear, was interpreted as due to the irreversible breakdown in the rigid structure built up of wax crystals in the oil below the pour point, whereas the high shear rate phenomenon is thought to be due to either molecular orientation or frictional heating effects, or both.

A mathematical analysis of frictional heating in a rotational viscometer was carried out and found to have an appreciable effect at high rates of shear, sufficient to account for a large part of the thixotropic effect. This analysis is presented in detail in Appendix D. As for the

* Throughout this report the term "thixotropy" is defined as a time or shear dependence of consistency or apparent viscosity, and not, as it is sometimes used, to mean general non-Newtonian flow characteristics.

breakdown at low shear rates, experiments were conducted on a synthetic blend of a pure hydrocarbon wax, n-octacosane, in Pennsylvania 150 Neutral oil. This blend, having a pour point above room temperature, was studied at 30° C in a modified Stormer viscometer with which the behavior of the oil at low shear rates could be studied much more precisely than with the Interchemical viscometer. This study revealed that under conditions where frictional heating of the oil could be neglected, the thixotropic effect was indeed irreversible, representing a permanent (within the time scale of the experiments, i.e., a few hours) decrease in viscosity of the oil due to shearing. An important finding in this study was that the decrease in viscosity of the oil due to shearing is a regular function of the work done in shearing.

Recent investigations, which are reported in the following sections of this report, have extended the studies with the modified Stormer viscometer to natural oils below their pour points at low temperatures. It will be seen that the rheological behavior of Pennsylvania 150 Neutral oil below the natural gel pour point is precisely the same as the behavior of the same oil artificially loaded with wax at higher temperatures. More precise measurements of the minimum sheared viscosity of this oil at low temperatures have permitted new calculations of the frictional heating effect at high rates of shear, which are in much closer agreement with data from the Interchemical viscometer than previously reported.

2. Experiments with the Modified Stormer Viscometer

Experiments with a synthetic blend of dewaxed 150 Neutral oil containing sufficient n-octacosane to produce a pour point above room

temperature demonstrated that the thixotropy, or decrease in viscosity due to shearing, was irreversible and an additive function of the work done in shearing (see Appendix D). None of the reversible apparent thixotropy observed for 150 Neutral at low temperatures during prolonged shearing at high shear rates in the Interchemical viscometer was observed. The next step in the research was to determine whether this behavior is typical of a wax-bearing oil having a pour point at low temperatures. Experiments were conducted on 150 Neutral oil having a pour point of +5° F (-15° C), which is the same oil used in the initial experiments with the Interchemical viscometer.

(a) Experimental Methods

For the purposes of these experiments the Stormer viscometer, modified according to Fischer[16] was adapted for low temperature use. Features of the adaptation on the Stormer viscometer itself are shown in Figure 20. The viscometer bath was insulated with glass wool and fitted with a lucite cover. The bob and bearing assembly were protected from atmospheric moisture by a glass sleeve which was flooded with dry nitrogen throughout the experiments. Isopropyl alcohol, used as a coolant, was circulated through the bath from an external cooling system.

Several systems for cooling and thermostating the bath liquid were tried. The two most satisfactory systems are shown diagrammatically in Figure 21. System A, which involves adjustment of the volume flow of the circulating liquid through coils in a dry ice-acetone bath and regulation by means of an intermittent heater operated through the control circuits of a Micromax recording potentiometer, gave satisfactory temperature control

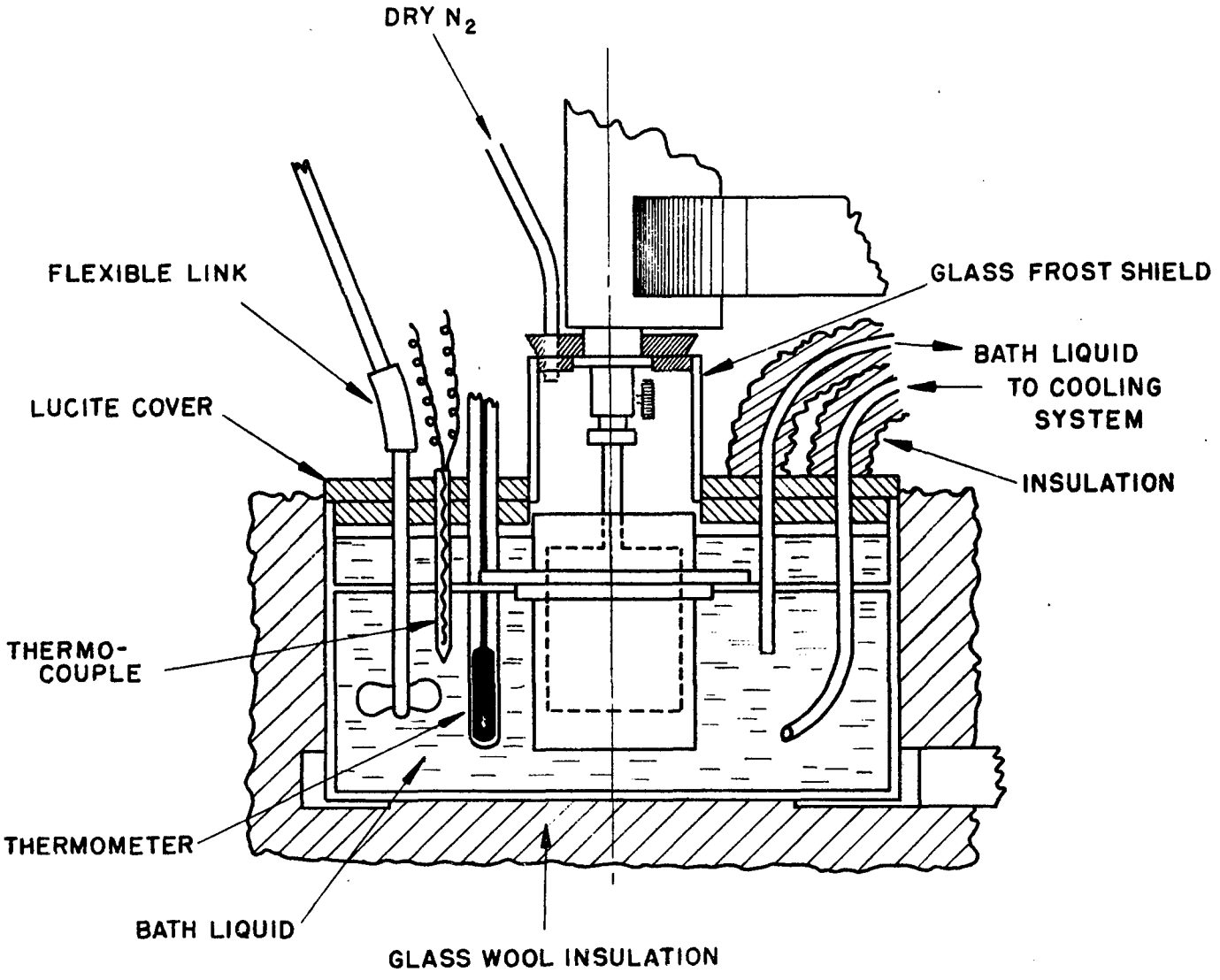
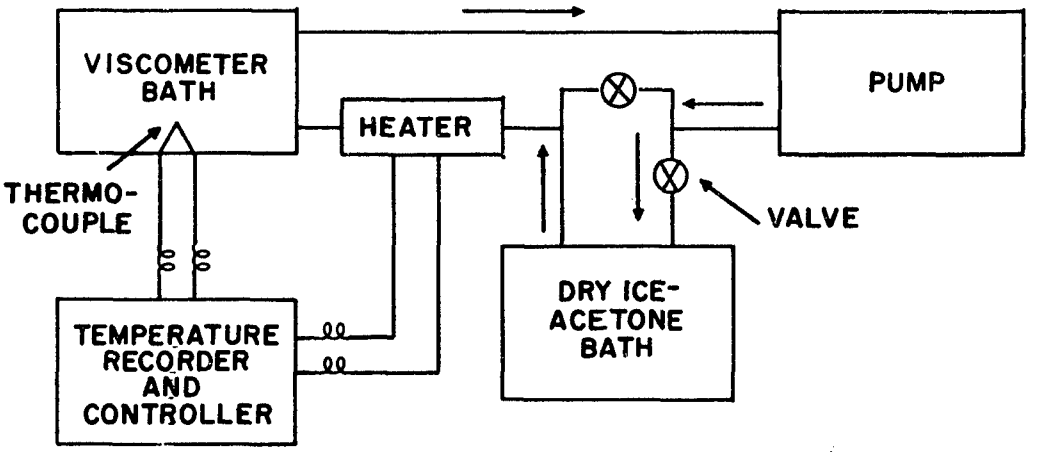
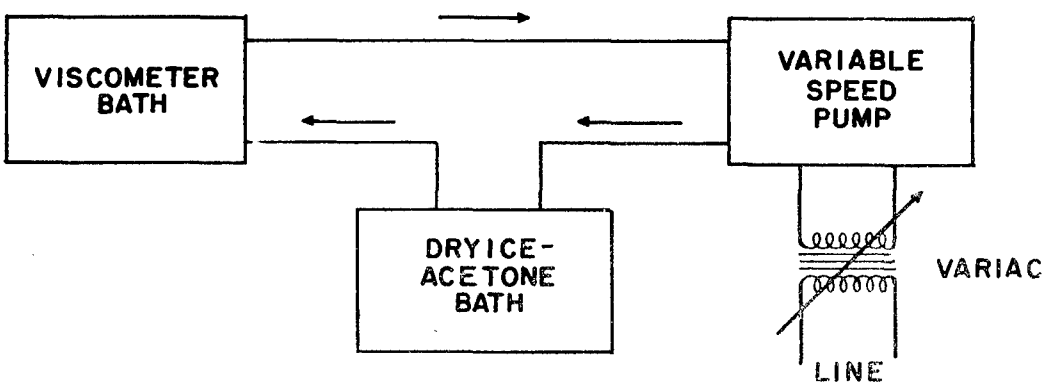


FIG. 20 – STORMER VISCOMETER MODIFICATIONS FOR LOW TEMPERATURE USE.



A. AUTOMATIC COOLING SYSTEM.



B. MANUAL COOLING SYSTEM.

FIG. 21-COOLING SYSTEMS FOR THE STORMER VISCOMETER.

of ± 0.1° C or better down to -20° C. System B, which is recommended for its simplicity, is entirely manual, but proved to be quite satisfactory to temperatures below -30° C. In the latter case temperature adjustment is made by means of a variac controlling the voltage on the motor of a centrifugal circulating pump.

The sample, first having been heated to 100° C, was placed in the viscometer cup, the bob set in place and the bath cooled to the temperature of the experiment. Unless otherwise noted, the sample was allowed to remain at the temperature of the experiment for thirty minutes before shearing was begun. Calculation of the cumulative work which had been done in shearing a sample was accomplished by keeping a careful record of the shearing history of the sample during an experiment. For any constant load, L, the number of revolutions, θ_L, of the viscometer bob at that load was recorded. This data is readily available since the Stormer viscometer incorporates a bob revolution counter. The total work of shearing in the time, t, is given approximately by the following:

(1) $$W = S\int_0^t \dot{e}(t)\, dt$$

Where: W = work done, in ergs/cm^3.

S = shearing stress, in dynes/cm^2.

$\dot{e}(t)$ = rate of shear, in sec^{-1}, which is a function of time.

Since: $$S = k_1 L$$

$$\dot{e} = k_2 \dot{\theta} \ ,$$

where k_1 and k_2 are instrumental constants[16] and θ is the bob speed, then

(2) $$W = k_1 k_2 L \int_0^t \dot{\theta}_L(t)\, dt$$

$$W = k_1 k_2 L \theta_L$$

(b) Shear Breakdown

Just as in the case of the synthetic blend, Pennsylvania 150 Neutral oil containing its natural waxes was found to exhibit an irreversible thixotropy which was a function of the work which had been done in shearing, irrespective of the load or shearing stress at which the work was done. Figure 3 shows the apparent viscosity plotted as a function of the work of shearing. As is necessarily the case with the Stormer viscometer, the shearing was not continuous, since after about 100 revolutions of the viscometer bob the line to which the load is attached must be rewound. Figure 22, then, shows the results of successive viscosity measurements plotted as a function of the cumulative work done in making the measurements. The fact that widely different loads corresponding to different shearing stresses were used and give points which fall on the same curve is proof that at any stage during shear breakdown the oil is a Newtonian fluid with a true coefficient of viscosity. If plastic flow exists, it is in the very early stages of breakdown. This point is further illustrated by the two consistency curves plotted from the data in Figure 22 and shown in Figure 23. These curves are linear through the origin as for Newtonian fluids. The curve representing an average work of shearing of 6×10^6 ergs/cm^3 shows a departure from linearity (broken line) which is due to the change in viscosity with the work expended in determining the curve.

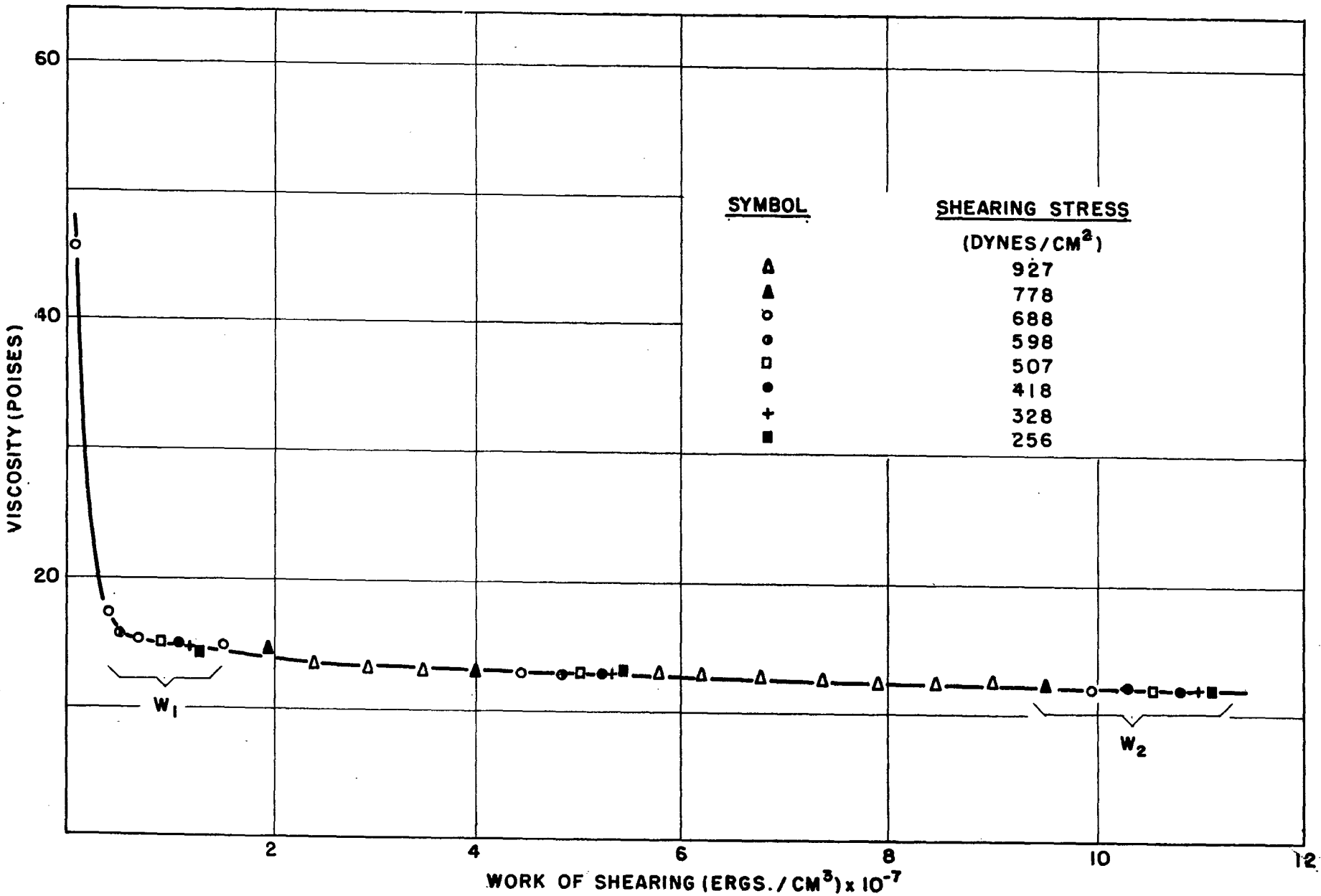


FIG. 22 — SHEAR BREAKDOWN OF PENN. 150 NEUTRAL OIL AT THE POUR POINT, -15°C (+5°F)

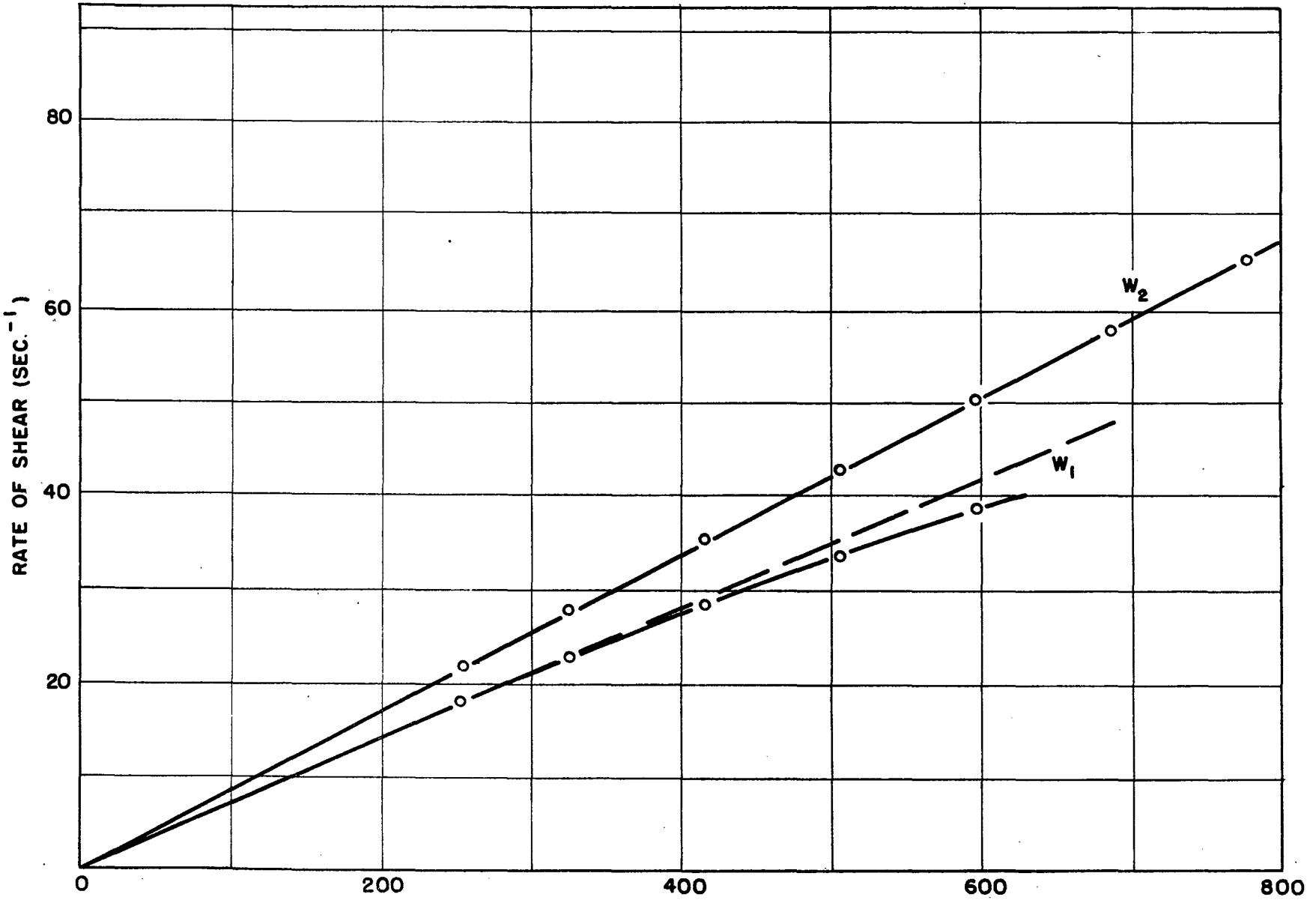


FIG. 23 - CONSISTENCY CURVES FOR PENN. 150 NEUTRAL OIL AT THE POUR POINT, −15°C (+5°F), AT PARTIAL AND COMPLETE BREAKDOWN. (DATA FROM FIG. 22)

The upper curve of Figure 23 represents the minimum sheared viscosity or the lowest viscosity which can be obtained as a result of shearing at -15° C. This curve, along with similar consistency curves for the oil at its minimum viscosity at -20° C and -25° C are shown in Figure 24. In all of these cases the oil in the completely sheared state is seen to be a Newtonian fluid with consistency curves which are linear through the origin.

Reference has been made to the irreversible nature of the shear breakdown of Pennsylvania 150 Neutral oil at low rates of shear. A careful investigation has shown that this is true only if the experiments are carried out under as nearly isothermal conditions as possible. The sensitivity of viscosity to slight temperature fluctuations at any stage of breakdown, and the dependence of viscosity on crystallization is shown in Figure 25. In this case shearing was begun after only 15 minutes soak, instead of the customary 30 minutes soak at the pour point. The liquid was evidently supercooled and crystallization was initiated by shearing. The viscosity rose at first and then began to drop with shearing in the customary manner. The effect of a temporary drop in temperature of 0.5° C and 1° C is shown. There was no increase in viscosity during 1.5 hours of no shearing at constant temperature.

The foregoing observations are readily explained if it is assumed that shear breakdown consists of degradation of a network of intergrown wax crystals, since a drop in temperature would cause new intergrowth from the saturated solution. Even at constant temperature one would expect slow recrystallization and an increase in viscosity over a period of several hours or days.

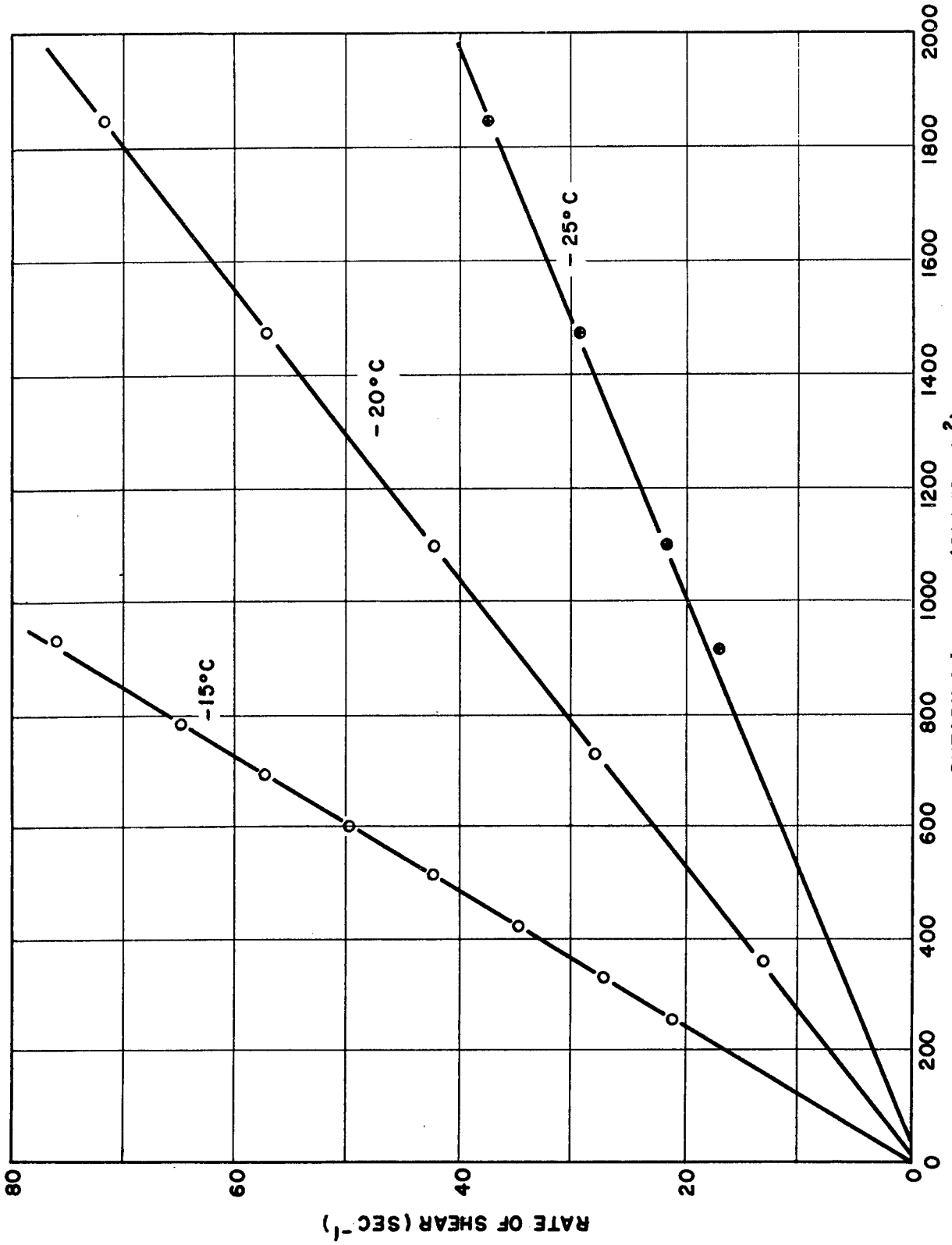


FIG. 24 – CONSISTENCY CURVES FOR PENN. 150 NEUTRAL OIL IN THE COMPLETELY SHEARED STATE BELOW THE POUR POINT.

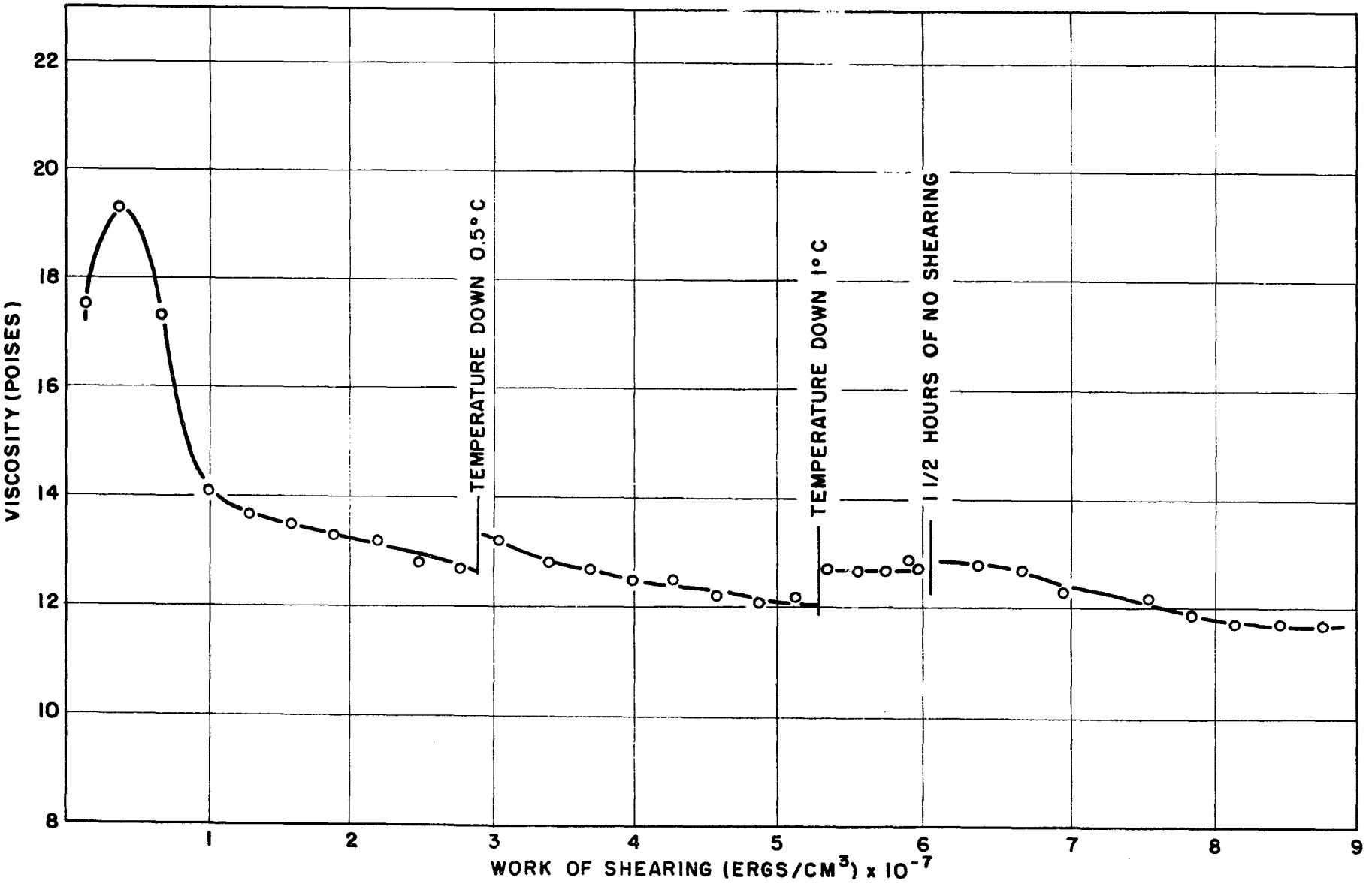


FIG. 25 - SENSITIVITY OF SHEARED VISCOSITY TO TEMPERATURE FLUCTUATIONS AND STANDING PENN. 150 NEUTRAL OIL AT THE POUR POINT, -15°C (+5°F)

(c) The Effect of a Pour Point Depressant

Early work with the Interchemical rotational viscometer demonstrated that the effect of a pour point depressant is to destroy the initial yield strength or high viscosity of the oil and drastically reduce its consistency[17]. The method of obtaining these curves was rather indirect and will be briefly reviewed here.

At high constant rates of shear typical relaxation curves were observed (Figure 26). This decrease in stress with time at constant rates of shear may be explained in part or wholly as due to frictional heating of the oil. At 50 sec^{-1} shear rate no such time effects were observed. The method of obtaining consistency curves representing the unsheared oil was to extrapolate the stress-time curves to zero time. This procedure is of dubious validity, since there is considerable uncertainty involved in the extrapolation. In any event, this procedure gives consistency curves, such as shown in Figure 27, which show that the consistency has been drastically reduced and no yield strength exists in the oil.

Consistency curves for the same oil, Pennsylvania 150 Neutral (pour point +5° F, -15° C), containing an effective depressant (in this case Acryloid 150) were carefully determined with the Stormer viscometer under conditions where frictional heating of the oil could be neglected. The results are shown in Figure 28 where it can be seen that at -20° C and -30° C the oil flows as a Newtonian fluid. No thixotropy was observed for

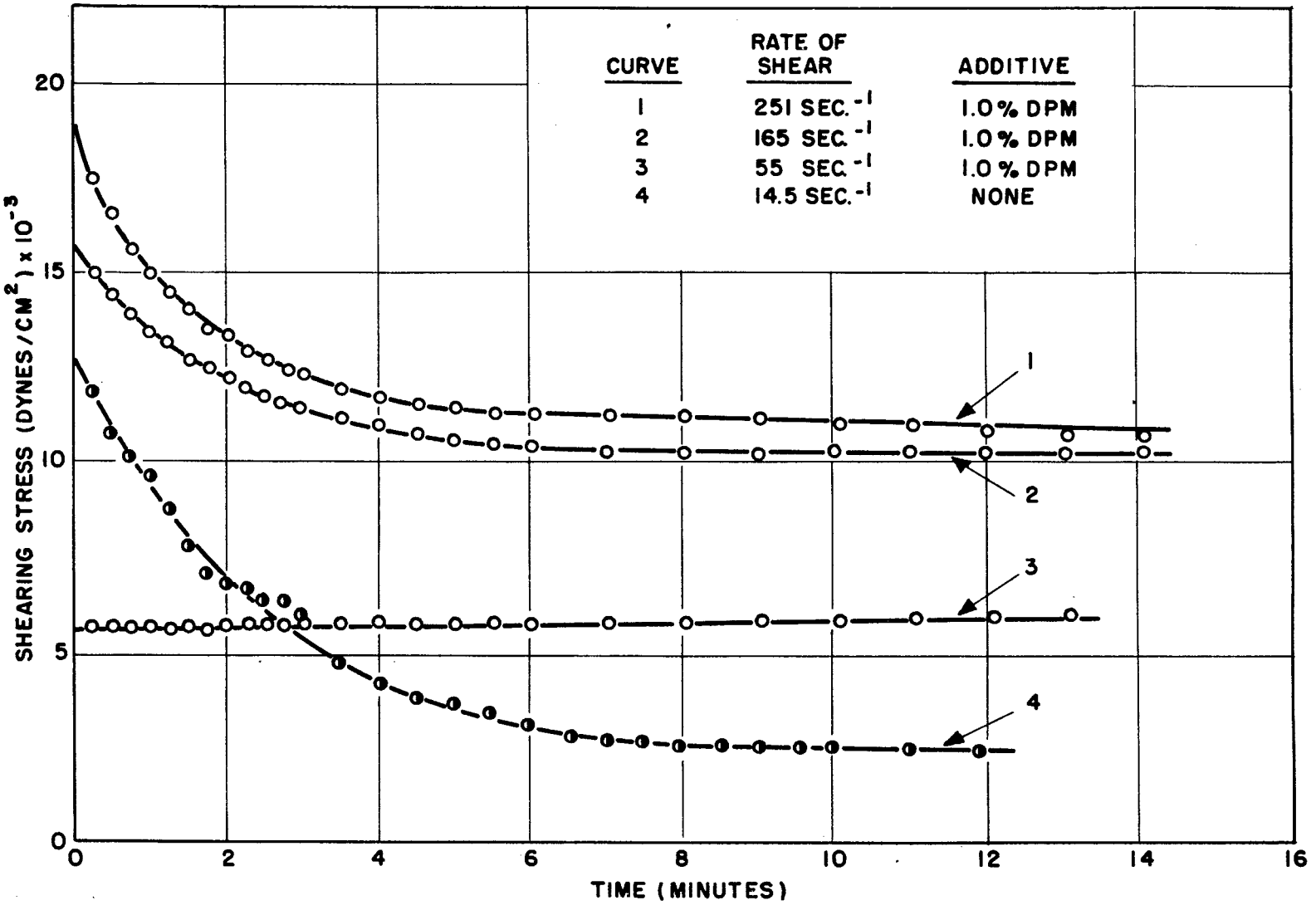


FIG. 26- STRESS – TIME CURVES FOR PENN. 150 NEUTRAL OIL (POUR POINT + 5°F), SHOWING THE UNTREATED OIL AND OIL CONTAINING 1.0% DODECYL POLYMETHACRYLATE AT −22°F (−30°C). DATA FOR UNTREATED OIL ARE FROM JONES AND TYSON[15]

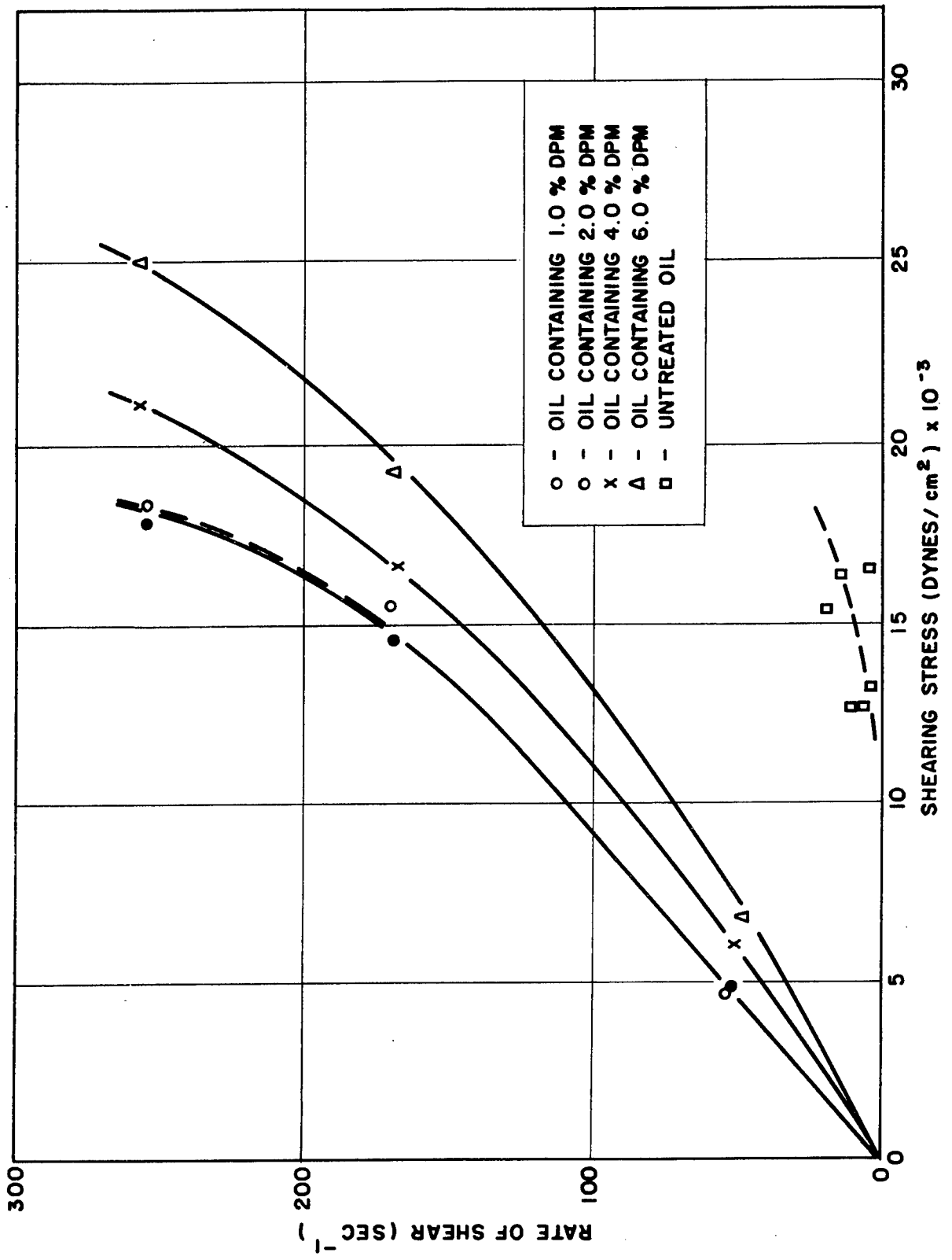


FIG.27- CONSISTENCY CURVES FOR UNSHEARED PENN. 150 NEUTRAL OIL OBTAINED BY EXTRAPOLATING STRESS-TIME CURVES TO ZERO TIME. THE UNTREATED OIL IS COMPARED WITH SAMPLES CONTAINING DODECYL POLYMETHACRYLATE AT -22°F (-30°C)

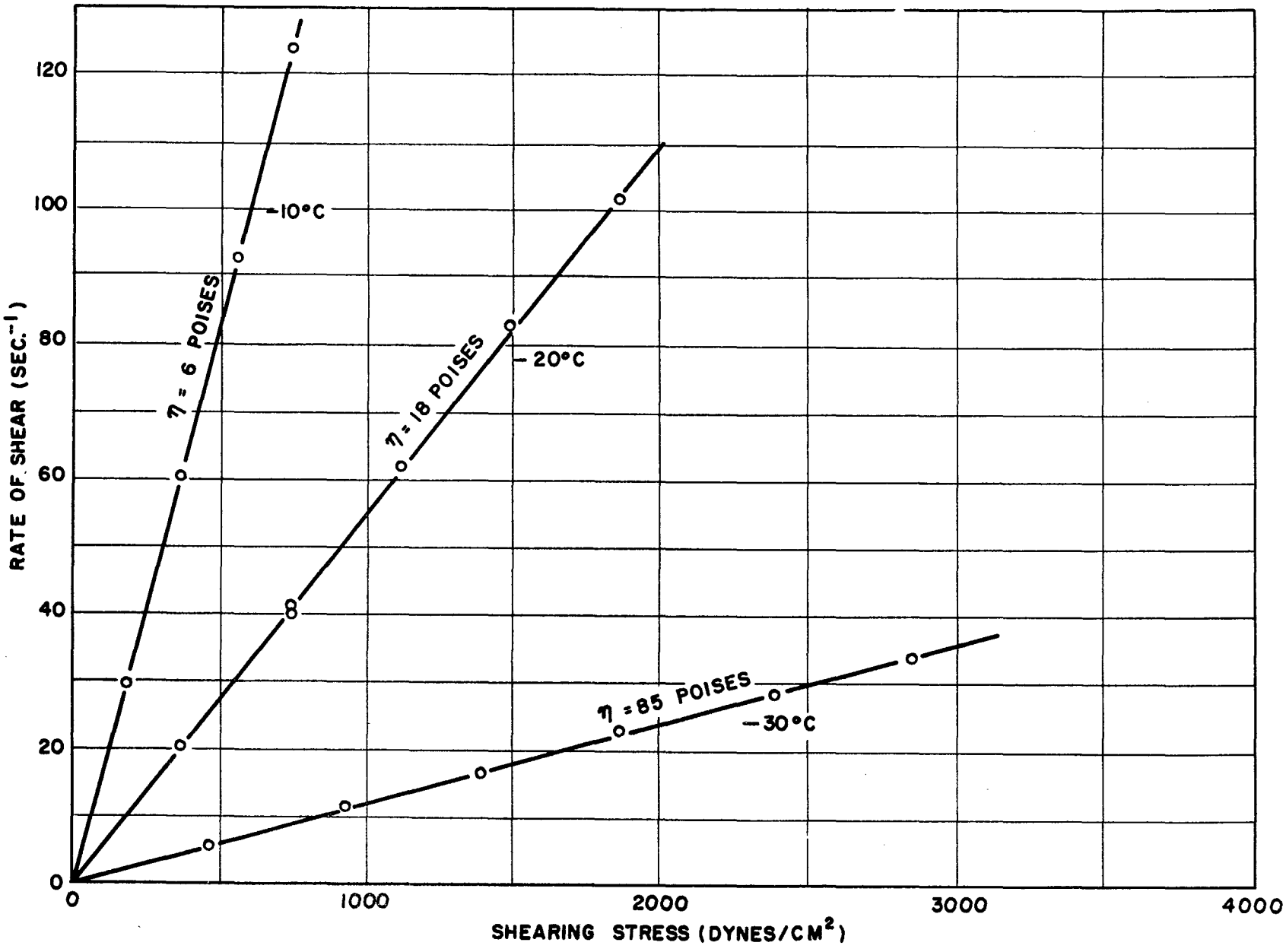


FIG. 28 – CONSISTENCY CURVES FOR PENN. 150 NEUTRAL OIL (POUR POINT, −15°C, +5°F) CONTAINING 1% ACRYLOID 150.

the oil containing the depressant, and there is no detectable curvature in the lines in Figure 28, however, the rates of shear are much lower than employed with the Interchemical viscometer.

The viscosity of the oil containing one per cent Acryloid 150 at -30° C, as determined with the Stormer viscometer is 85 poises. A calculation of the viscosity in the limit of low rates of shear from data with the Interchemical viscometer (Figure 27) gives 90 poises for the oil containing one per cent dodecyl polymethacrylate at -30° C. This agreement is considered satisfactory since in the latter case the concentration of pure polymer is greater than for Acryloid 150 which is an oil solution of polymer.

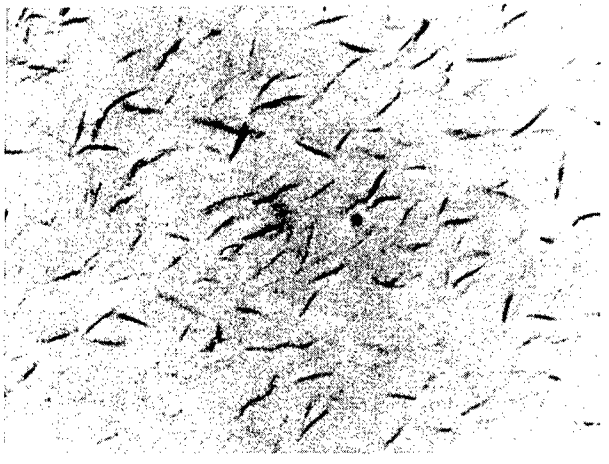
3. Mechanics of Breakdown

From earlier work it has been proposed that the shear breakdown of 150 Neutral oil and its blends with wax is due to a mechanical degradation of the wax network which forms a rigid structure through intergrowth and/or interlocking of the thin wax crystals. A direct check on this theory was made with the cold stage microscope.

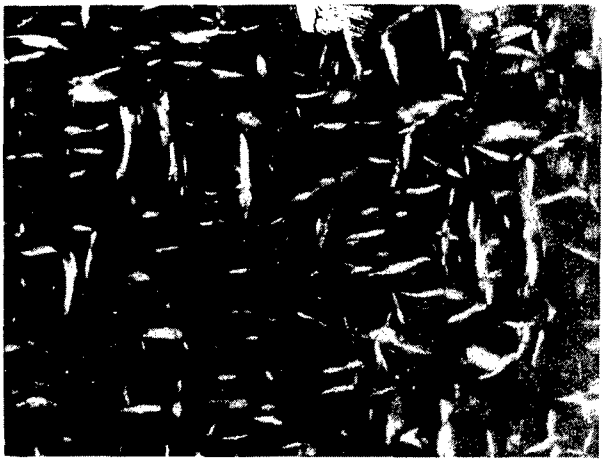
A device was constructed as to permit direct observation of a thin layer of oil being sheared between two microscope slides mounted on the microscope cold stage. This simple device consisted of a plastic mount to hold the lower slide in place and permit movement of the upper slide back and forth in a plane normal to the optical axis of the microscope. The oil film thickness was maintained at 0.1 mm by means of brass runners cemented to the lower slide.

Photomicrographs of Pennsylvania 150 Neutral, pour point 30° F (-1° C), at 23° F (-5° C) are shown in Figure 29. Figures 29A and B show the undisturbed oil in the same field as seen with bright illumination and crossed nicols, respectively. These two photomicrographs of the same field give quite different impressions. In bright illumination the sample appears to consist of a layer-like structure of very thin plates, the edges of which are dark (Figure 29A), while between crossed nicols these dark areas are double refracting with diffuse birefringent areas in the interior of the plates (Figure 29B). This appearance, which might easily be taken for needles, is explained by Rhodes, Mason and Sutton[18] who found plates in slack waxes from Pennsylvania oils to be extremely thin and curled at the edges, isotropic when viewed flatwise and double refracting when edgewise or inclined.

Figure 29C shows the wax network in the early stages of shearing. In the photomicrograph, which is devoid of motion, it is difficult to detect the phenomenon, however, the upper left portion of the field is still an immobile network while the crystals in the lower right are detached and move during shear. The boundary between the rigid and mobile portions of the oil is evidenced by a slight crowding of crystals near the center of the field. Figure 29D shows the appearance of the crystals after vigorous shearing. The rigid network is completely destroyed and the crystal fragments move independently, although one small aggregate of crystals may still be seen. This progressive degeneration of the rigid network into smaller and smaller aggregates and finally into single crystal fragments parallels the progressive decrease in viscosity as the rigid mass is sheared.



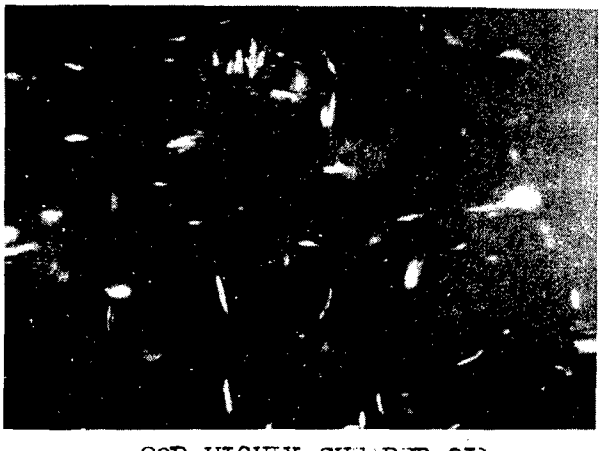
29A UNSHEARED OIL
(BRIGHT ILLUMINATION)



29B UNSHEARED OIL
(CROSSED NICOLS)



29C MODERATELY SHEARED OIL
(CROSSED NICOLS)



29D HIGHLY SHEARED OIL
(CROSSED NICOLS

FIG. 29 SHEARING OF PENNSYLVANIA 150 NEUTRAL OIL (POUR POINT 30° F) AT 23° F

MAGNIFICATION 100 X

Although a quantitative treatment of the relation between the work of shearing and the viscosity of the oil has not been made and does not seem practical, a qualitative explanation is readily available. The relation between concentration of suspended particles and viscosity of the suspension is given by the well-known Einstein equation,

$$\eta = \eta_0 (1 + k C_v) , \tag{3}$$

where η and η_0 are the viscosities of the suspension and pure liquid, respectively, C_v is the volume concentration of particles and k is a constant which depends on the shape of the particles, being 2.5 for spheres, which shows its order of magnitude. This equation applies to dilute suspensions where interaction between the particles is neglected.

In the case of an aggregate of wax crystals the oil held within the aggregate is immobilized and thus contributes to the volume concentration of particles, C_v. Thus, as crystals break off from the aggregates during shearing the effective volume concentration of suspended material is steadily reduced with an accompanying decrease in viscosity according to equation (3).

In the completely sheared state where the wax crystals are individually dispersed, only the actual volume of the wax in suspension contributes to increasing the viscosity. From experience with synthetic blends it can be estimated that not more than two or three per cent wax in suspension is required to produce a pour point. Thus, from equation (3) it can be roughly estimated that the viscosity of the completely sheared oil at the pour point is not more than 10 per cent greater than the viscosity

the oil would have if the suspended wax were not present. This point is illustrated by Figure 30 which shows a smooth curve through the data for viscosities above the pour point and the completely sheared viscosities below the pour point for Pennsylvania 150 Neutral oil.

Viscosity data for the oil containing pour point depressants is also plotted in Figure 30. It can be seen that these viscosities are comparable with the minimum viscosities for the sheared oil below the pour point. This is consistent with the theory that the function of the pour point depressant is just to cause the wax crystals to grow individually and prevent intergrowth. The result is that the wax crystals are individually dispersed and do not form adherent aggregates or a rigid network. The effect of shearing is to reduce the aggregated wax to this same state.

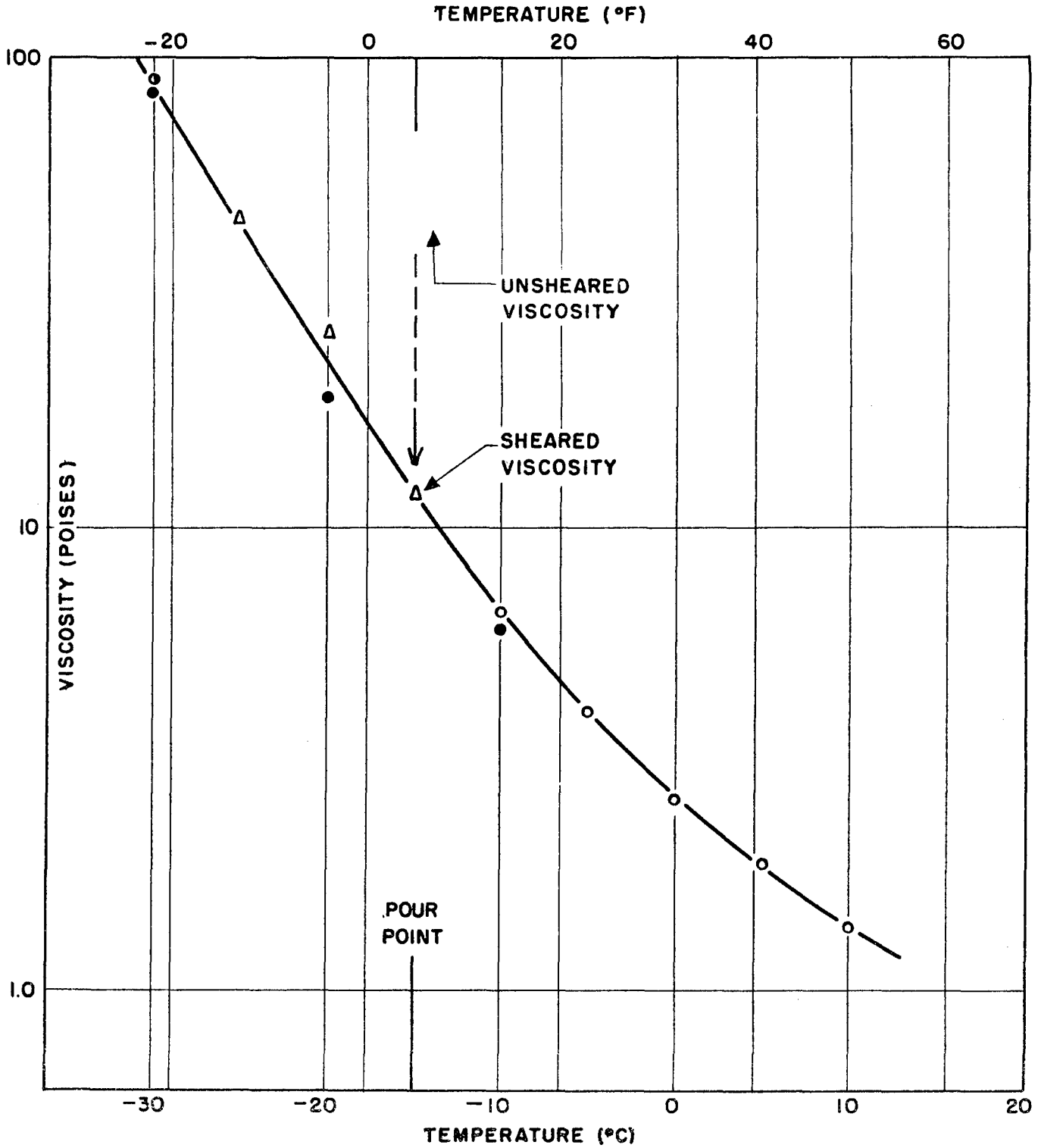
As for the rate of viscosity decrease with work input, a simple empirical expression has been found to fit the data for a number of oils and synthetic blends reasonably well. The viscosity as a function of work of shearing, such as shown in Figure 20 for Pennsylvania 150 Neutral at its pour point, -15° C (+5° F), appears to be an hyperbola of the form:

(4) $$\eta = A + B'/W ,$$

Where η is the work-dependent viscosity, W is the work input, and A and B' are constants. Since at infinite work input, η is just equal to A, then A is the minimum sheared viscosity, η_∞. Equation (4) may be rewritten in the form:

(5) $$\eta = \eta_\infty (1 + B/W),$$

Where the constant B has the dimensions of work and determines the rate of breakdown.



- o VISCOSITY ABOVE THE POUR POINT
- Δ MINIMUM SHEARED VISCOSITY BELOW THE POUR POINT
- ● OIL + 1% ACRYLOID 150
- ⊛ OIL + 1% DODECYL POLYMETHACRYLATE

FIG. 30 - MINIMUM VISCOSITY VS. TEMPERATURE FOR PENN. 150 NEUTRAL OIL

The formula, equation (5), is based on the assumption that at any stage of breakdown the oil behaves as a Newtonian fluid, i.e., no yield value, and that in the initial, unsheared condition the viscosity is infinite. These assumptions are probably not strictly valid, however, for high work inputs at least the first condition is usually met. Figure 31 shows the fit obtained with equation (5) and the data for two oils of different final viscosities and at different temperatures. Curve A is a dewaxed Pennsylvania 150 Neutral (pour point +30° F, -1° C) at -4° C (25° F), and curve B represents a blend containing six per cent n-octacosane and 3.5 per cent hexadecyl polymethacrylate in dewaxed Pennsylvania 150 Neutral, at 25° C (77° F) slightly below its pour point. The fit of the equation for the latter oil is excellent, possibly due to the fact that much better temperature control was possible at 25° C than at the lower temperature.

Minimum sheared viscosities and the constant B for the shear breakdown of several oils and blends are given in Table 38. Both the natural oils and synthetic blends exhibit similar shear breakdown characteristics with comparable values for B, which seem to increase with increasing viscosity. The blend containing the pour point depressant is of interest since this concentration of wax is on the borderline of depressing activity for the depressant (see Figure 14).

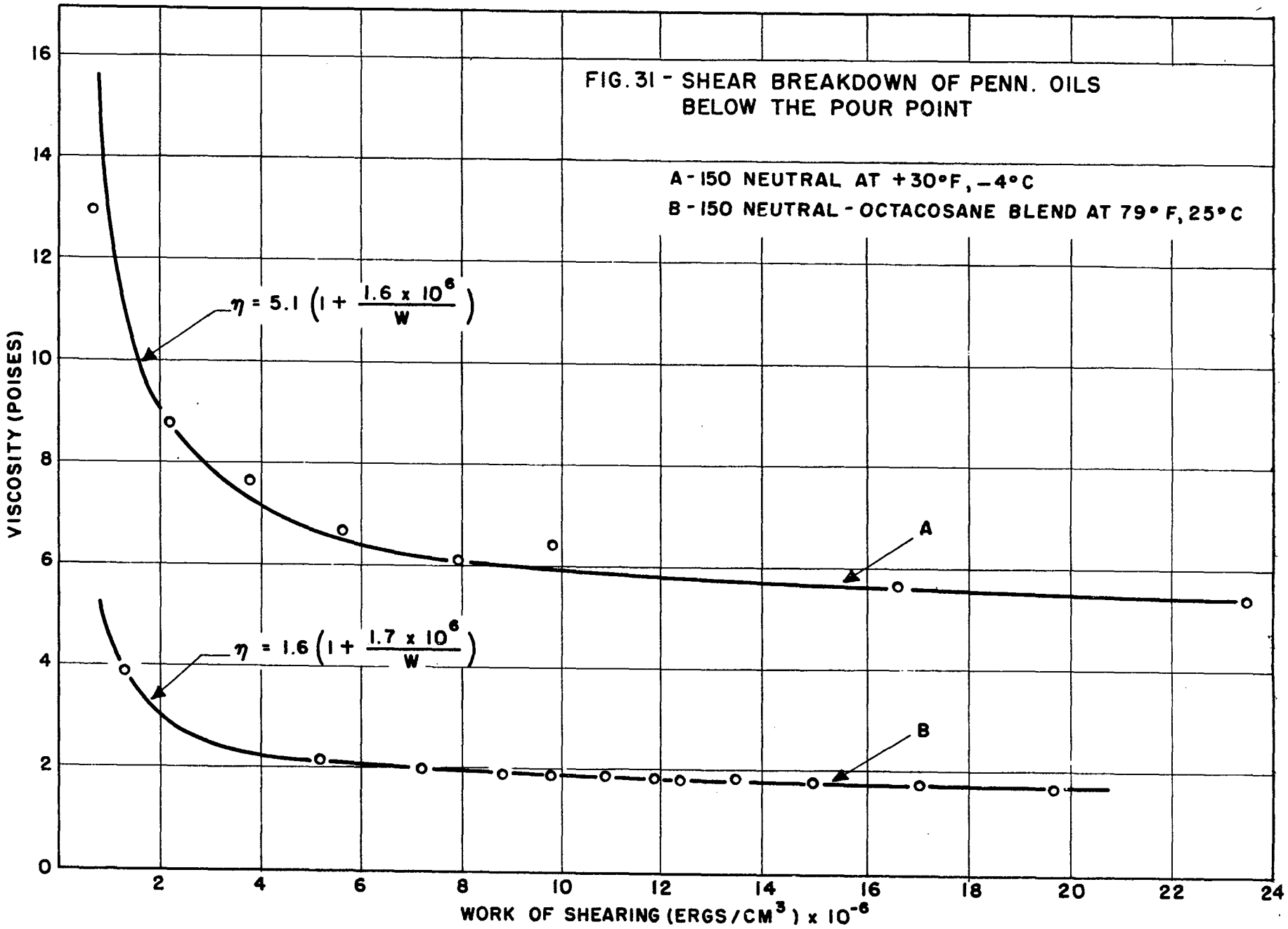

FIG. 31 - SHEAR BREAKDOWN OF PENN. OILS BELOW THE POUR POINT
A - 150 NEUTRAL AT +30°F, -4°C
B - 150 NEUTRAL - OCTACOSANE BLEND AT 79° F, 25° C
$\eta = 5.1\left(1 + \frac{1.6 \times 10^6}{W}\right)$
$\eta = 1.6\left(1 + \frac{1.7 \times 10^6}{W}\right)$
A
B
VISCOSITY (POISES)
WORK OF SHEARING (ERGS/CM^3) x 10^{-6}
0
2
4
6
8
10
12
14
16
18
20
22
24

Table 38

SHEAR BREAKDOWN DATA FOR LUBRICATING OILS AND BLENDS

Oil	Pour Point (°F)	Temperature (°F)	η_∞ (Poises)	$B/10^6$ (ergs/cm^3)
150 Neutral	5	5	12.0	2.4
150 Neutral	30	25	5.1	1.6
150 Neutral Blend*	78	77	1.6	1.7
Bright Stock Blend**	>77	77	17.6	7.2

*6 per cent n-octacosane, 3.5 per cent hexadecyl polymethacrylate in dewaxed 150 Neutral

**4 per cent n-octacosane in Bright Stock

4. Frictional Heating Effects

The effect of frictional heating on the measurement of viscosity with the rotational viscometer has been analyzed in the earlier work on this project. A detailed theoretical treatment of the heat flow and temperature distribution in the oil at thermal and mechanical equilibrium is given in Appendix D, and the resulting effect on viscosity measurements with the Interchemical viscometer is estimated in a previous publication[14] which is also included in the Appendix. It was concluded that a large part of the reversible thixotropic effect observed at high rates of shear was due to frictional heating of the oil, however, the observed effect was much larger than could be accounted for on this basis alone. These calculations were based on estimates of the minimum sheared viscosity for Pennsylvania 150 Neutral oil at -25° and -30° C. Considerable uncertainty was involved in these estimates, and from the more extensive measurements which have been made at low rates of shear with the Stormer viscometer, it is now known that the minimum sheared viscosity of the oil is about 50 per cent lower than previously estimated. A recalculation of frictional heating effects is, therefore, now in order.

Previous estimates which were based on the slope of the equilibrium consistency curves in the limit of low rates of shear gave 220 and 90 poises for the viscosity at -30° and -25° C, respectively. From the data in Figure 30, obtained with the Stormer viscometer, it can be seen that these values should be about 85 and 40 poises for -30° and -25° C, respectively. The original error can be attributed to a number of factors: (1) the uncertainty of the slope of the consistency curves in the limit of low rates

of shear, (2) the fact that the precision of the Interchemical viscometer is least at low cup speeds, and (3) the fact that the oil may not have been sheared to its minimum viscosity at low rates of shear. It thus appears that all the data obtained with the Interchemical viscometer for rates of shear less than 100 sec^{-1} (Figure 82, Appendix D) does not represent the viscosity of the completely sheared oil and should be discarded.

Using the more correct data obtained with the Stormer viscometer, the effect of frictional heating on the measured values of viscosity will now be calculated. At thermal equilibrium the measured viscosity, η, is given by:

( ) $$\eta = \eta_o \sqrt{\frac{2}{\beta}} \frac{\sinh^{-1}\sqrt{\beta/2}}{\sqrt{1 + \beta/2}}$$

where η_o = the true viscosity at the reference temperature

$$\beta = \frac{\alpha \eta_o d^2}{\kappa} \left(1 + \frac{d}{R_b}\right) \dot{e}^2$$

d = cup to bob clearance distance

R_b = radius of the viscometer bob

$\dot{e}$ = rate of shear

κ = thermal conductivity of the oil

$$\alpha = \frac{\ln \eta_2 - \ln \eta_1}{T_1 - T_2}$$ = temperature coefficient of viscosity

Using the values for η_o of 85 and 40 poises for -30° and -25° C, respectively, gives a value for α of 0.15° C^{-1}. The thermal conductivity is taken as 1.47×10^{4} ergs/cm sec°C. Results for the 0.1 and 0.2 cm cup to bob clearances at -30° C are shown in Figure 32 compared with experimental

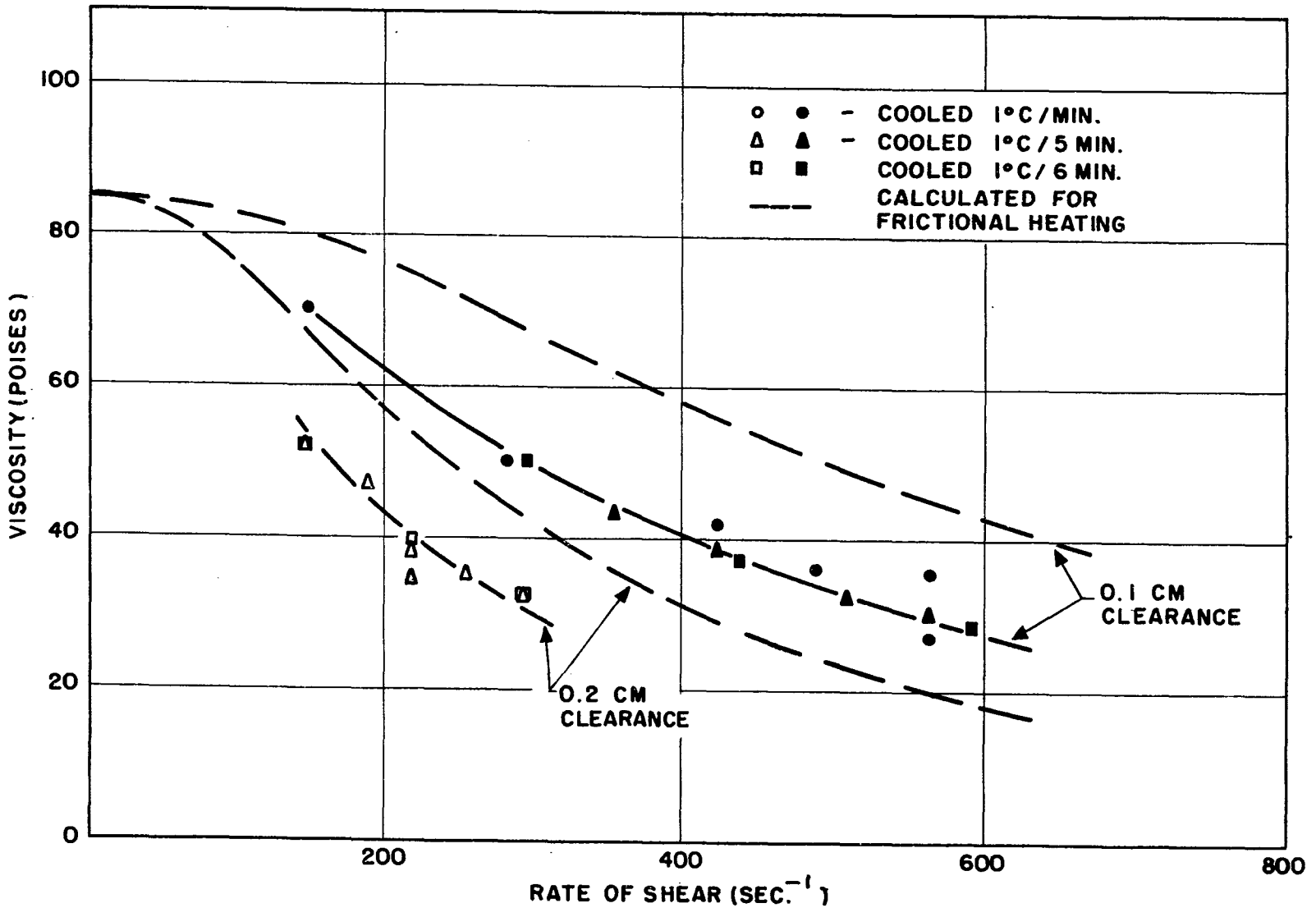


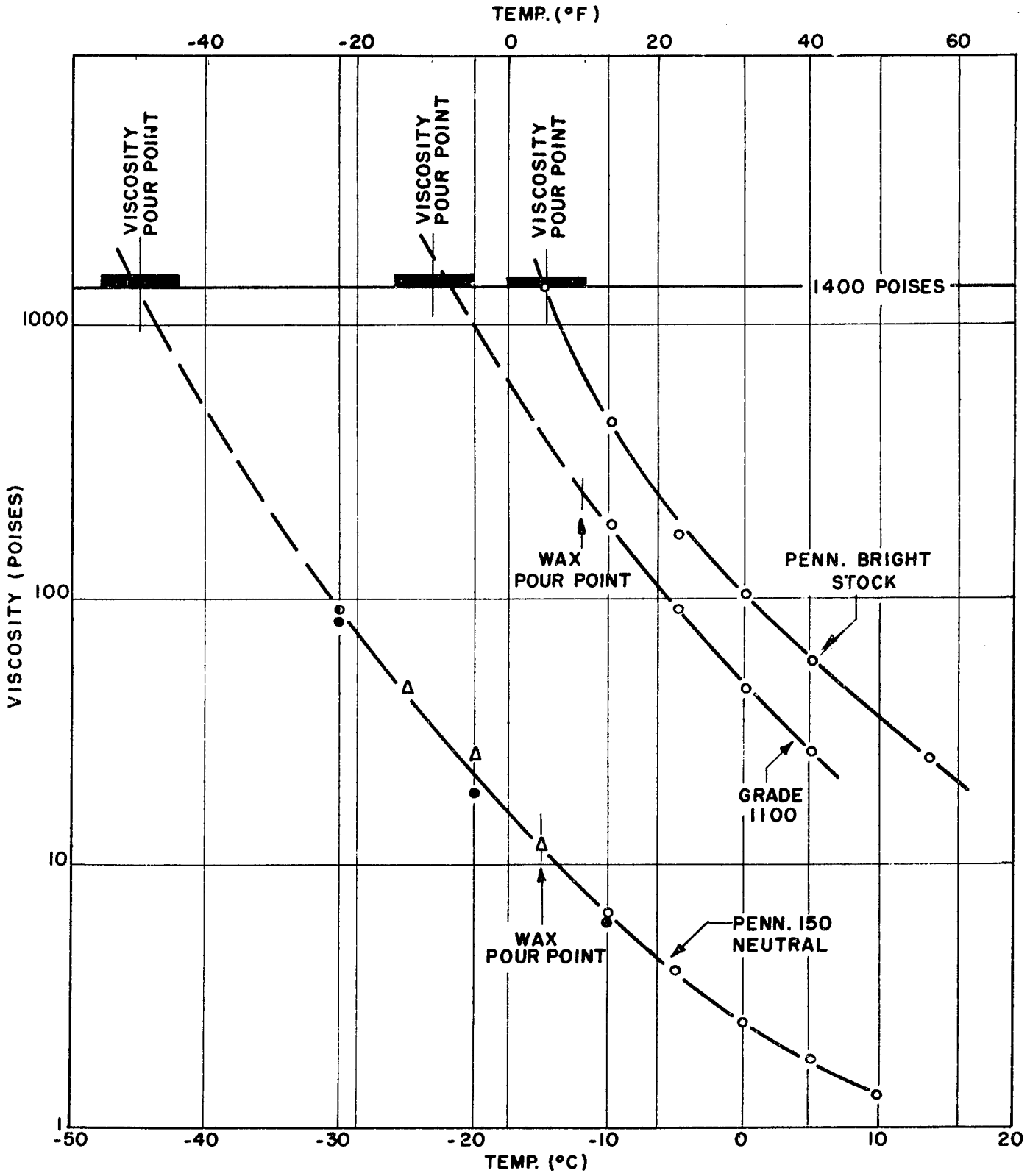
FIG. 32 - EQUILIBRIUM VISCOSITIES OBSERVED WITH THE INTERCHEMICAL VISCOMETER AND CALCULATED FOR FRICTIONAL HEATING. PENN. 150 NEUTRAL OIL AT −30°C

results from the Interchemical viscometer for rates of shear above 100 sec^{-1}. The agreement of experimental results with theory for frictional heating is much better than previously reported. There is as yet, however, not sufficient agreement to state that all the thixotropic effect at high rates of shear is due to frictional heating.

B. Viscosity Pour Points

The foregoing discussion of the rheology of lubricating oils below their pour points has been concerned with oils which solidify due to wax gelation. This phenomenon is apparently independent of the viscosity of the oil. It is apparent, however, that since the viscosity of liquids increases rapidly with decreased temperature, an oil which does not gel will at some temperature have a viscosity so high that it will not pour according to the standard ASTM pour point test.

A case in point is that of one of the base stocks used in this study, a Pennsylvania Bright Stock dewaxed to the same pour point as the 150 Neutral oil. The viscosity-temperature curve for this oil as determined with the Stormer rotational viscometer at temperatures down to the pour point is shown in Figure 33. No thixotropic effects were observed and the oil appeared to be a Newtonian fluid with a viscosity of about 1400 poises at the pour point. No pour point depressant tried was effective in reducing the pour point of this oil. Since the function of a depressant is to prevent the formation of a wax gel, it follows that a pour point depressant cannot be effective if the pour point is not due to wax gelation. The most effective pour point depressant cannot, therefore,



○ VISCOSITY ABOVE POUR POINT
Δ MINIMUM SHEARED VISCOSITY
● OIL + 1% ACRYLOID 150
◐ OIL + 1% DODECYL POLYMETHACRYLATE

FIG. 33 – VISCOSITY – TEMPERATURE CURVES AND VISCOSITY POUR POINTS FOR VARIOUS PETROLEUM OILS.

reduce the pour point of a wax-bearing oil below the viscosity pour point of the oil. This sets a lower limit on the effectiveness which can be expected from pour point depressants.

Figure 33 includes viscosity-temperature data for Pennsylvania 150 Neutral oil and a grade 1100 aircraft oil above the pour point. For the former, minimum sheared viscosities and viscosities in the presence of pour point depressants below the pour point are included. The lowest pour point obtained with depressants in 150 Neutral oil was -50° F (-46° C) (four per cent dodecyl polymethacrylate), while with grade 1100 oil, Acryloid 150 produced a pour point of -10° F (-24° C). From Figure 33 it can be seen that a reasonable extrapolation of the viscosity-temperature data passes through these minimum pour point temperatures (within the limit of error of the pour point method) at about 1400 poises, indicating that these minimum pour points are due to oil viscosity and are the lowest pour points which can be obtained with pour point depressants alone. It is, therefore, possible to predict with reasonable accuracy the lowest pour point possible for a given undiluted oil. For this purpose, kinematic viscosities would be more appropriate. However, as demonstrated in Figure 33, absolute viscosities probably give a sufficiently close approximation of the viscosity pour point.

C. Grade 1100 Aircraft Oil

The rheological properties of a grade 1100 oil, a service aircraft oil, has recently been given special attention. This oil, which represents a blend of Bright Stock and lighter crude fractions was found to exhibit a somewhat more complex flow behavior than encountered with Pennsylvania

150 Neutral and its synthetic blends. The oil studied was a Mid-Continent grade 1100 oil, untreated, meeting MIL-L-6082-A specifications. The pour point of this oil is +10° F (-12° C).

Consistency curves (shearing stress vs rate of shear) for this oil were determined at four temperatures, +5°, 0°, -5°, and -10° C, above the pour point and at two temperatures, -14.6° and -16.6° C, below the pour point. These consistency curves, shown in Figure 34, exhibit features both above and below the pour point which were not observed in studies on Pennsylvania 150 Neutral.

Above the pour point at lower temperatures, -5° and -10° C, there is a departure from linearity of the consistency curves, corresponding to pseudo plastic instead of Newtonian flow. For this type of flow the apparent viscosity decreases with increasing rates of shear. This type of flow is common for solutions of large molecules, i.e., high polymers, and it is not unreasonable to expect that this oil, containing a large proportion of the heavy Bright Stock molecules, might also behave in this way.

This pseudo plastic behavior of grade 1100 aircraft oil confirms the findings of Umstatter[19] who reported that mixtures of Bright Stock and lighter oils exhibit the same type of flow. That author shows that such flow behavior increases the load carrying capacity of the lubricant some two to three fold, by evening out the pressure and temperature distribution in a bearing.

Below the pour point the grade 1100 oil did not exhibit the marked thixotropy or shear breakdown characteristics observed for Pennsylvania 150 Neutral oil. Here, again, consistency curves were determined with the

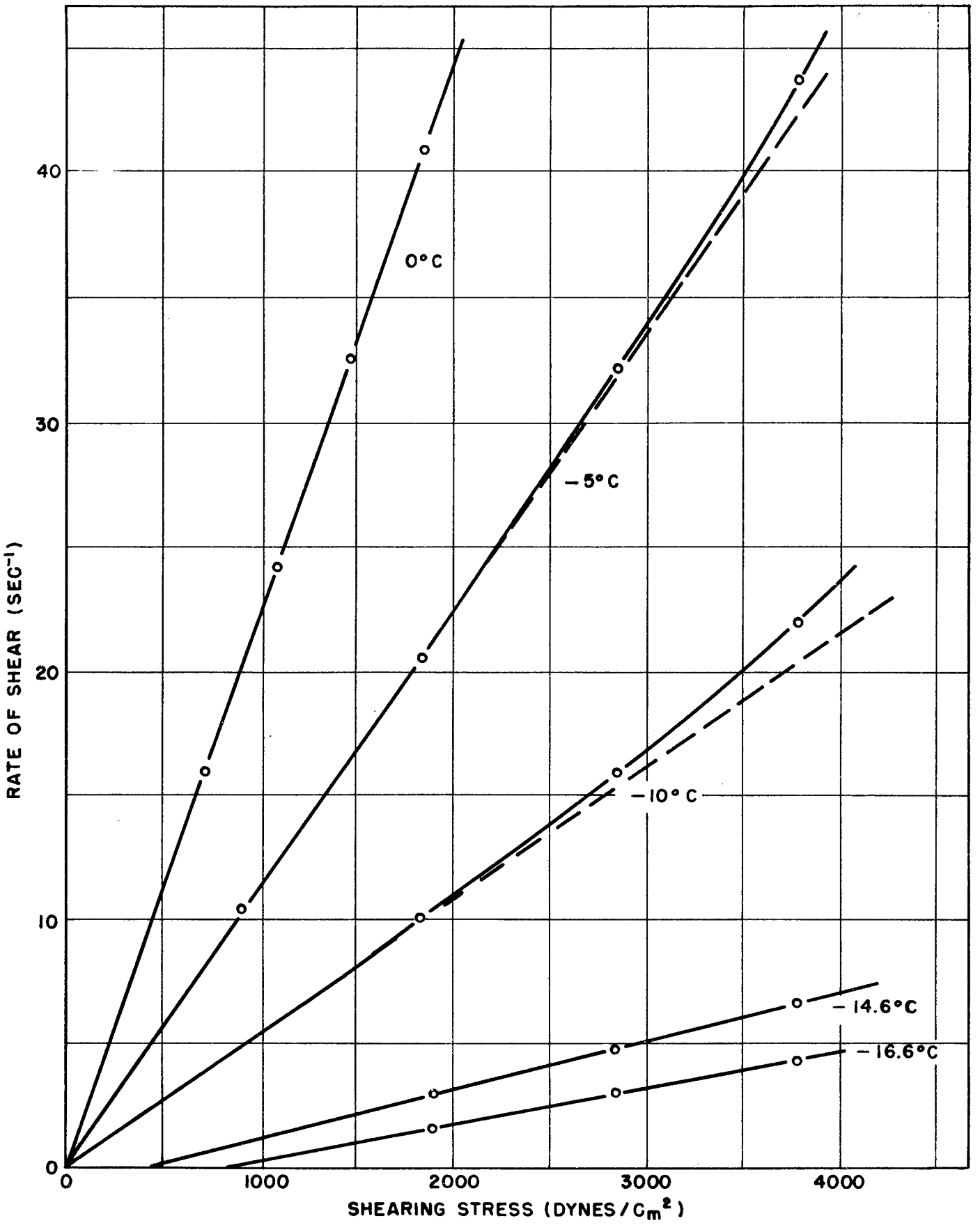


FIG. 34 - CONSISTENCY CURVES FOR GRADE 1100 AIRCRAFT OIL
(POUR POINT -12°C, +10°F)

modified Stormer viscometer where the measurements are made at constant shearing stresses, and the breakdown in structure is evidenced by a change in bob speed with time. Figure 35 shows the number of bob revolutions plotted as a function of time for successive measurements with three different shearing stresses, 3780, 1910 and 2840 dynes/cm^2, in that order, at -14.6° C, 2.6° C below the pour point, on an initially unsheared oil. The bob speed, which is the slope of these curves, shows a marked increase during initial shearing at 3790 dynes/cm^2, but thereafter remains independent of time for the limited amount of shearing required for the determinations. Similar behavior was observed for the same sample cooled to -16.6° C. These limited data indicate plastic flow with a yield strength of about 300 and 700 dynes/cm^2 at -14.6° and-16.6° C, respectively (Figure 34), and a relative stability to shear breakdown, at least under mild conditions of shearing. The explanation for this behavior, which is in contrast to that of Pennsylvania 150 Neutral oil and its wax blends below the pour points, is lacking. The need for future research in the low temperature rheology of lubricants is, however, clearly indicated.

IX. RECOMMENDATIONS

With regard to the development of so-called "pour point depressants" to increase the flowability of oil at low temperatures, evidence has been presented to show that pour point depressants act only to prevent wax-oil gelation. The limitation to the effectiveness of a pour point depressant is, therefore, described by the viscosity pour point of the base stock

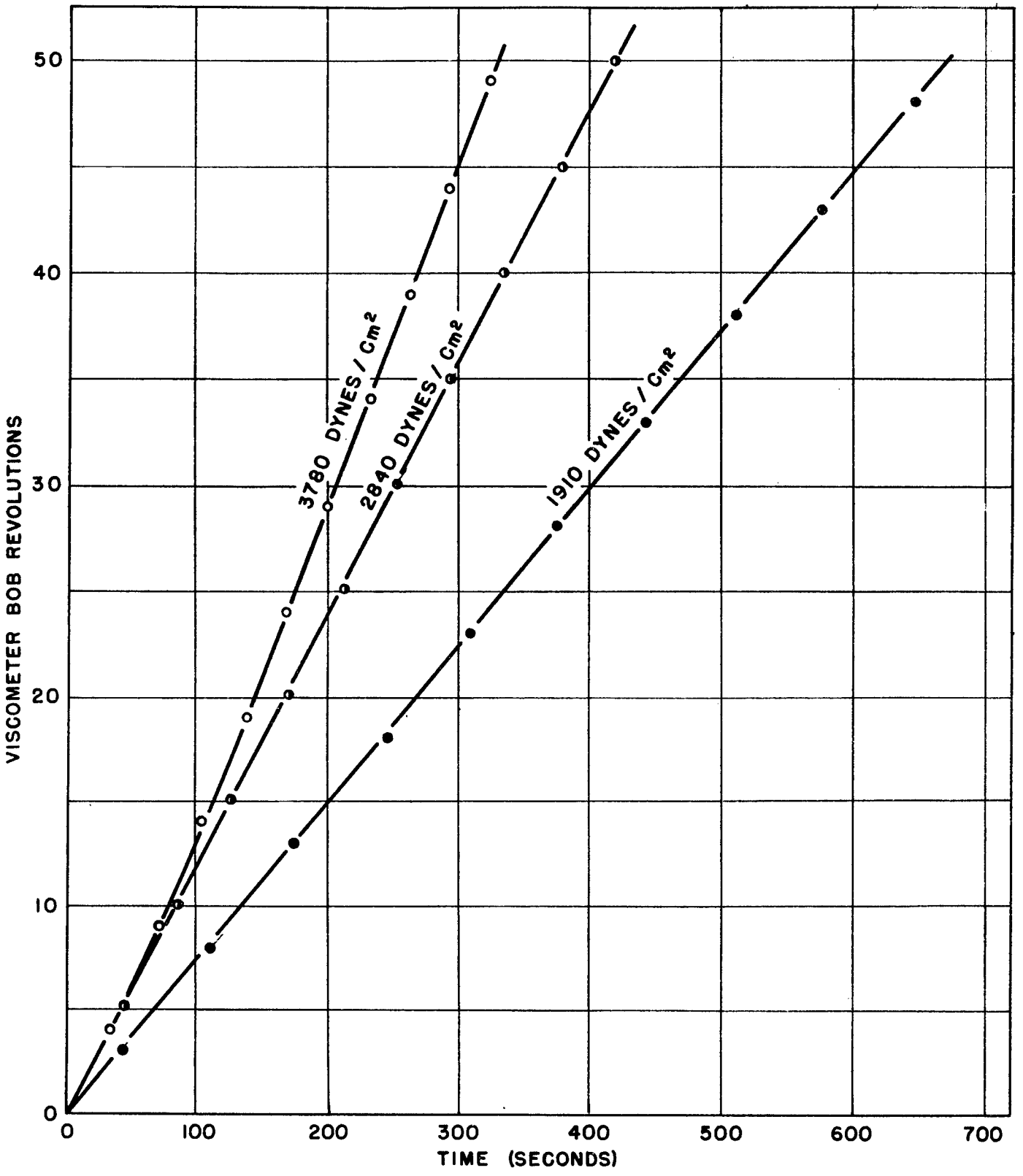


FIG. 35 – BOB REVOLUTIONS VS. TIME FOR GRADE 1100 OIL IN THE MODIFIED STORMER VISCOMETER BELOW THE POUR POINT
(TEMPERATURE = -14°C, +8°F)

under consideration in the absence of wax-oil gelation. The depressants now available commercially already show this maximum effect when used within specified concentrations. Work directed to the enhancing of the pour depressing effect is, therefore, unwarranted.

However, a general program for the synthesis of pour point depressants could be undertaken for other, perhaps equally cogent, reasons. The structural requirements of pour point depressants have been elucidated clearly enough to permit the synthesis of materials possessing a wide variety of functional groups. These have been used in the preparation of one new material, poly-1,2-hexadecylene phthalate. Others could be prepared for the following purposes:

1. To lower the necessary additive concentration. The present specification calls for a maximum pour point depressant concentration of one per cent. It is possible that the magnitude of use of pour point depressants is sufficient to warrant attempting to lower additive costs by achieving the maximum additive effect at a lower concentration.

2. To improve other important additive properties such as thermal stability, shear stability, hydrolytic stability, etc.

Within the scope of this project rheology has served the function of helping to elucidate the nature of the gel structure in wax-bearing oils and has thus contributed to an understanding of the mechanism of pour point depression by additives. In addition, much needed information has been obtained and techniques of study developed relative to the flow behavior of lubricants at low temperatures. These data are sufficient to demonstrate that wax-bearing oils and heavy lubricants are non-Newtonian fluids at low temperature and that the coefficient of viscosity does not have its

conventional meaning. A thorough understanding of the rheology of lubricants at low temperatures is thus a necessary prelude to future considerations of improved flow characteristics at low temperatures and improvement of viscosity index. The application of rheology to the study of the following specific problems is, therefore, recommended for consideration in future research programs:

1. Pour Point Reversion

The techniques developed on this project for the quantitative description of the thixotropic properties of oils below their pour points may be fruitfully applied to the study of the change in effectiveness of pour point depressants in oils subjected to cyclic temperature changes.

2. Viscosity Index Improvers

In this field, not only rheology but also its ally, colloid chemistry, may be applied to advantage. The concept of viscosity index should be reviewed in the light of the non-Newtonian flow characteristics of high polymer solutions. For many such solutions, the apparent viscosity at a given temperature is not constant, but is dependent on shearing stress, and, therefore, viscosity index may be without real significance. Useful viscosity-temperature data should come from a knowledge of the true consistency of the oil as obtained by the methods of rheology. The consistency of solutions of high polymers in petroleum oils is strongly influenced by configurational changes of the polymer molecules with changes in temperature. Approached from this point of view, a study of the improvement of the consistency-temperature characteristics of petroleum oils should lead to new and improved additives and possibly the tailoring of oils for specific applications.

X. NOTEBOOK REFERENCES

The work described in this report can be found in the following notebooks: B-1478, B-1491, B-1560, B-1564, B-1567, B-1687, B-1691, B-1754, B-1788, B-1854, B-1893, B-1903, B-1933, B-1945, B-1946, B-1981, C-1305, C-1308, C-1311, C-1312, C-1314, C-1327, C-1331, C-1344, C-1549, C-1639, C-1842, C-1964, C-2038, C-2091, C-2151, C-2182, C-2205, C-2295, C-2322, C-2375, C-2453; Microscopy 0017-1701, 1736, 1755, 1773, 1789, 1831.

XI. ACKNOWLEDGMENTS

The following tabulation shows the distribution of responsibility for the work carried out:

Project Leader	February 10, 1949 to April 15, 1950	Glen W. Hedrick
Project Leader	April 15, 1950 to November 1, 1952	Gilbert Gavlin
Literature Survey		G. Corcoran
Analysis of Commercial Additives		G. Corcoran and E. Swire
Synthesis of Additives		E. Swire
Crystallographic Studies of Wax in Lubricating Oil		E. Swire
Rheology of Petroleum Hydrocarbons		S. P. Jones

Other contributing personnel are: R. L. Bond, J. E. Barkley, L. U. Berman, R. Bloomquist, A. J. Court, G. Costa, I. Corvin, R. Crouse, J. Collins, R. Congino, J. Cook, R. Conkling, B. Cygan, E. Grimm. H. B. Gausebeck, R. J. Havlik, J. Hogan, J. R. James, M. Jeffreys, R. Kircher, G. R. Kopshever, M. Kayner, A. M. Kingsley, D. Landon, E. Lieber, C. H.

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XIII. APPENDIX

A. Evaluation of Commercial Additives

Viscosity, Viscosity Index, and Pour Point Data

		Table No.	Page
1.	**Paraffin Wax - White Oil Blend**		
a.	Paraflow PDX	39	138
b.	Santopour B	40	139
c.	Pourex	41	140
d.	Santopour C	42	141
e.	Acryloid 150	43	142
f.	Santopour	44	143
g.	Paraflow 46X	45	144
h.	Santolube 203A	46	145
i.	Acryloid 710	47	146
j.	Santodex	48	147
k.	Acryloid HF 600	49	148
l.	Low Molecular Weight Polybutene	50	149
m.	High Molecular Weight Polybutene	51	150
n.	Acryloid 722	52	151
o.	Paratone	53	152
p.	Vinyl Ether Resin	54	153
2.	**Microcrystalline Wax - White Oil Blend**		
a.	Santopour B	55	154
b.	Pourex	56	155
c.	Santopour C	57	156
d.	Paraflow 46X	58	157
e.	Santopour	59	158
f.	Paraflow PDX	60	159
g.	Acryloid 710	61	160
h.	Santolube 203A	62	161
i.	Acryloid 150	63	162
j.	Santodex	64	163
k.	Acryloid HF 600	65	164
l.	Low Molecular Weight Polybutene	66	165
m.	High Molecular Weight Polybutene	67	166
n.	Acryloid 722	68	167
o.	Paratone	69	168
p.	Vinyl Ether Resin	70	169
3.	**Microcrystalline - Paraffin-White Oil Blend**		
a.	Santopour B	71	170
b.	Paraflow PDX	72	171

		Table No.	Page
c.	Santopour C	73	172
d.	Santopour	74	173
e.	Pourex	75	174
f.	Paraflow 46X	76	175
g.	Santolube 203A	77	176
h.	Acryloid 150	78	177
i.	Acryloid 710	79	178
j.	Santodex	80	179
k.	Acryloid HF 600	81	180
l.	High Molecular Weight Polybutene	82	181
m.	Low Molecular Weight Polybutene	83	182
n.	Acryloid 722	84	183
o.	Paratone	85	184
p.	Vinyl Ether Resin	86	185
4.	Bright Stock - Pennsylvania		
a.	Paraflow PDX	87	186
b.	Acryloid 710	87	186
c.	Santopour	88	187
d.	Paratone	88	187
e.	Santodex	89	188
f.	Santopour C	89	188
g.	Acryloid 150	90	189
h.	Paraflow 46X	90	189
i.	Santolube 203A	91	190
j.	Vinyl Ether Resin	91	190
k.	Pourex	92	191
l.	Low Molecular Weight Polybutene	92	191
m.	High Molecular Weight Polybutene	93	192
n.	Santopour B	93	192
o.	Acryloid 722	94	193
p.	Acryloid HF 600	94	193
5.	Bright Stock - Mid-Continent		
a.	Acryloid 150	95	194
b.	Santopour B	96	195
c.	Santopour C	97	196
d.	Santopour	98	197
e.	Paraflow 46X	99	198
f.	Santolube 203A	100	199
g.	Pourex	101	200
h.	Paraflow PDX	102	201
i.	Paratone	103	202
j.	30% Vinyl Ether Resin in Oil	104	203
k.	Acryloid 710	105	204

		Table No.	Page
l.	Acryloid 722	106	205
m.	Acryloid HF 600	107	206
n.	Santodex	108	207
o.	High Molecular Weight Polybutene	109	208
p.	Low Molecular Weight Polybutene	110	209
6.	150 Neutral - Pennsylvania		
a.	Acryloid 150	111	210
b.	Paraflow PDX	112	211
c.	Santopour C	113	212
d.	Paraflow 46X	114	213
e.	Santopour B	115	214
f.	Santopour	116	215
g.	Pourex	117	216
h.	Acryloid 722	118	217
i.	Santolube 203A	119	218
j.	High Molecular Weight Polybutene	120	219
k.	Low Molecular Weight Polybutene	121	220
l.	Santodex	122	221
m.	Paratone	123	222
n.	Acryloid 710	124	223
o.	Acryloid HF 600	125	224
p.	Vinyl Ether Resin	126	225
7.	150 Neutral - Mid-Continent		
a.	Paraflow PDX	127	226
b.	Santopour	128	227
c.	Paraflow 46X	129	228
d.	Acryloid 150	130	229
e.	Santopour B	131	230
f.	Santopour C	132	231
g.	Pourex	133	232
h.	Santolube 203A	134	233
i.	Acryloid 722	135	234
j.	30% Vinyl Ether Resin in Oil	136	235
k.	Paratone	137	236
l.	Acryloid HF 600	138	237
m.	Santodex	139	238
n.	Low Molecular Weight Polybutene	140	239
o.	High Molecular Weight Polybutene	141	240
p.	Acryloid 710	142	241
8.	Mineral Seal Oil - Pennsylvania		
a.	Santopour B	143	242
b.	Paraflow 46X	144	243
c.	Paraflow PDX	145	244

		Table No.	Page
d.	Santolube 203A	146	245
e.	Acryloid 150	147	246
f.	Pourex	148	247
g.	Santopour	149	248
h.	Santopour C	150	249
i.	Low Molecular Weight Polybutene	151	250
j.	High Molecular Weight Polybutene	152	251
k.	Vinyl Ether Resins	153	252
l.	Paratone	154	253
m.	Acryloid 710	155	254
n.	Acryloid 722	156	255
o.	Acryloid HF 600	157	256
p.	Santodex	158	257
9.	Cadet Z Oil		
a.	Paraflow 46X	159	258
b.	Paraflow PDX	160	259
c.	Acryloid 150	161	260
d.	Santopour C	162	261
e.	Santopour	163	262
f.	Santolube 203A	164	263
g.	Santopour B	165	264
h.	Pourex	166	265
i.	Paratone	167	266
j.	Acryloid 710	168	267
k.	Acryloid 722	169	268
l.	Acryloid HF 600	170	269
m.	Santodex	171	270
n.	Low Molecular Weight Polybutene	172	271
o.	High Molecular Weight Polybutene	173	272
p.	30% Vinyl Ether Resin	174	273

Table 39

PARAFLOW PDX

Sample No.	94	95	96	97	98	99
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-
Per cent Wax added	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-20	-20	-40	-35	-40	-35
Cloud Point (°F)	42	42	44	38	36	38
Viscosities						
Centistokes						
100°	24.72	24.96	26.13	28.04	29.8	32.54
130°	-	-	-	-	-	-
210°	4.43	4.47	4.6	4.82	5.11	5.46
Saybolt Univ. Seconds						
100°	117.7	118.7	123.8	132.4	140.0	152.2
210°	40.76	40.88	41.3	42.02	42.95	44.08
Viscosity Index	96.1	97.6	98.6	101.4	100.4	114.8

Table 40

SANTOPOUR B

Sample No.	256	257	258	259	260	261
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-
Per cent wax added	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-15	-30	-	-45	-
Cloud Point (°F)	-	46	40	-	36	-
Viscosities						
Centistokes						
100°	-	24.53	24.85	-	26.3	-
130°	-	-	-	-	-	-
210°	-	4.41	4.53	-	4.67	-
Saybolt Univ. Seconds						
100°	-	116.9	118.3	-	124.6	-
210°	-	40.69	41.08	-	41.53	-
Viscosity Index	-	95.82	105.4	-	103.9	-

Table 41

POUREX

Sample No.	202	203	204	205	206	207
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-
Per cent Wax added	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-20	-25	-	-25	-
Cloud Point (°F)	-	45	42	-	46	-
Viscosities						
Centistokes						
100°	-	24.72	25.17	-	27.27	-
130°	-	-	-	-	-	-
210°	-	4.41	4.49	-	4.13	-
Saybolt Univ. Seconds						
100°	-	117.7	119.7	-	128.9	-
210°	-	40.69	40.95	-	41.73	-
Viscosity Index	-	93.49	97.49	-	100.1	-

Table 42

SANTOPOUR C

Sample No.	184	185	186	187	188	189
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-
Per cent Wax added	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-20	-20	-	-35	-
Cloud Point (°F)	-	38	36	-	38	-
Viscosities						
Centistokes						
100°	-	24.62	28.9	-	42.5	-
130°	-	-	-	-	-	-
210°	-	4.67	5.32	-	7.95	-
Saybolt Univ. Seconds						
100°	-	117.3	136.1	-	197.0	-
210°	-	41.53	43.63	-	2.2	-
Viscosity Index	-	121.0	129.3	-	146.3	-

Table 43

ACRYLOID 150

Sample No.	10	12	13	14	15	16	17	18
Base	White Oil C*	-	-	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-	-	-
Per cent Wax added	0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	0	0	0.5	1.0	3.0	5.0	10.0	15.0
Pour °F	+15°	+15°	-25°	-20°	-20	-20	-20	-15
Cloud °F	+18°	+48°	+46°	+46°	+44	+42	+40	+40
Viscosity °F								
Centistokes								
100°	-	24.2	26.5	26.7	34.45	40.2	57.6	91.4
130°	-	-	-	-	-	-	-	-
210°	-	4.4	4.8	4.92	6.5	7.36	10.89	16.9
Saybolt Univ. Seconds								
100°	119.8	115.5	125.5	126.2	160.7	186.6	266.4	422.3
130°	-	-	-	-	-	-	-	-
210°	40.9	40.6	41.95	42.34	47.43	50.24	62.35	85.3
Viscosity Index	95.2	97.75	113.6	120.9	141.7	142.2	148.1	149.8

*White Oil C was refined by Sinclair Refining Company from Mid-Continent Stock.

Table 44

SANTOPOUR

Sample No.	58	59	60	61	62	63
Base Oil	White Oil C	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-
Per cent Wax added	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour °F	+5	-15°	-20°	-20°	-25°	-20°
Cloud °F	+42°	+40°	+38°	+38°	+38°	+36°
Viscosity °F						
Centistokes						
100°	24.38	24.55	25.17	25.4	26.9	28.3
130°	-	-	-	-	-	-
210°	4.42	4.47	4.57	4.6	4.80	4.93
Saybolt Univ. Seconds						
100°	116.2	118.0	119.6	120.7	127.5	133.4
130°	-	-	-	-	-	-
210°	40.72	40.88	41.2	41.27	41.95	42.39
Viscosity Index	98.68	102.6	105.9	105.4	109.8	108.7

Table 45

PARAFLOW 46X

Sample No.	39	40	41	42	43	44
Base Oil	White Oil C	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-
Per cent Additive	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour °F	-15°	-20°	-15°	-20°	-15°	-15°
Cloud °F	+40	+42	+40	+36	+36	+36
Viscosity °F						
Centistokes						
100°	24.64	24.86	25.9	26.65	27.11	32.65
130°	-	-	-	-	-	-
210°	4.46	4.54	4.64	4.79	4.85	5.5
Saybolt Univ. Seconds						
100°	117.4	118.3	122.9	126.2	128.1	152.6
130°	-	-	-	-	-	-
210°	40.85	41.02	41.43	41.9	42.12	44.36
Viscosity Index	100.24	103.6	105.06	111.1	112.3	118.06

Table 46

SANTOLUBE 203-A

Sample No.	292	293	294	295	296	297
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-
Per cent Wax Added	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-10	-10	-	-10	-
Cloud Point (°F)	-	40	38	-	44	-
Viscosities Centistokes						
100°	-	24.64	25.00	-	26.64	-
130°	-	-	-	-	-	-
210°	-	4.43	4.54	-	4.7	-
Saybolt Univ. Seconds						
100°	-	117.4	118.9	-	126.2	-
210°	-	40.76	41.1	-	41.6	-
Viscosity Index	-	96.85	104.7	-	103.4	-

Table 47

ACRYLOID 710

Sample No.	112	113	114	115	116	117
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-
Per cent Wax added	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	+15	+10	0	-10	-15	-15
Cloud Point (°F)	48	50	50	46	48	46
Viscosities						
Centistokes						
100°	25.47	26.75	31.44	37.15	53.54	71.13
130°	-	-	-	-	-	-
210°	4.63	4.93	5.94	7.08	10.35	13.98
Saybolt Univ. Seconds						
100°	121.0	126.6	147.3	172.9	247.7	328.6
210	41.4	42.38	45.63	49.3	60.44	73.83
Viscosity Index	108.6	121.4	140.3	147.0	151.1	151.5

Table 48

SANTODEX

Sample No.	166	167	168	169	170	171
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-
Per cent Wax added	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	20	20	-	25	-
Cloud Point (°F)	-	42	44	-	42	-
Viscosities						
Centistokes						
100°	-	26.18	30.36	-	48.72	-
130°	-	-	-	-	-	-
210°	-	4.73	5.51	-	8.89	-
Saybolt Univ. Seconds						
100°	-	124.1	142.5	-	225.5	-
210°	-	41.73	44.24	-	55.42	-
Viscosity Index	-	110.7	129.6	-	145.8	-

Table 49

ACRYLOID HF 600

Sample No.	148	149	150	151	152	153
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-
Per cent Wax added	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	+25	+20	+20	+20	+20	+20
Cloud Point (°F)	42	44	44	44	42	44
Viscosities						
Centistokes						
100°	24.71	26.55	30.52	34.88	43.49	60.27
130°	-	-	-	-	-	-
210°	4.74	4.91	5.8	6.77	9.94	12.9
Saybolt Univ. Seconds						
100°	117.6	125.8	143.2	162.7	201.5	278.7
210°	41.76	42.31	45.18	48.30	59.01	69.72
Viscosity Index	125.7	129.8	140.1	148.3	161.2	156.1

Table 50

LOW MOLECULAR WEIGHT POLYBUTENE

Sample No.	220	221	222	223	224	225
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-
Per cent Wax added	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (^{o}F)	-	25	26	-	25	-
Cloud Point (^{o}F)	-	46	44	-	44	-
Viscosities						
Centistokes						
100°	-	25.14	32.14	-	55.08	-
130°	-	-	-	-	-	-
210°	-	4.51	5.65	-	9.18	-
Saybolt Univ. Seconds						
100°	-	119.5	150.4	-	254.8	-
210°	-	41.01	44.69	-	56.4	-
Viscosity Index	-	99.88	125.5	-	138.4	-

Table 51

HIGH MOLECULAR WEIGHT POLYBUTENE

Sample No.	238	239	240	241	242	243
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-
Per cent Wax added	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	25	25	-	30	-
Clour Point (°F)	-	46	46	-	46	-
Viscosities						
Centistokes						
100°	-	26.87	33.13	-	51.36	-
130°	-	-	-	-	-	-
210°	-	4.78	5.77	-	8.42	-
Saybolt Univ. Seconds						
100°	-	127.2	154.8	-	237.6	-
210°	-	41.89	45.08	-	53.8	-
Viscosity Index	-	108.5	125.8	-	134.7	-

Table 52

ACRYLOID 722

Sample No.	130	131	132	133	134	135
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	+25	20	25	15	25	25
Cloud Point (°F)	44	46	46	44	48	46
Viscosities						
Centistokes						
100°	26.25	26.23	29.78	33.82	56.54	60.13
130°	-	-	-	-	-	-
210°	4.76	4.78	5.56	6.29	10.88	11.45
Saybolt Univ. Seconds						
100°	124.4	124.3	139.9	157.9	261.5	278.0
210°	41.82	41.89	44.4	46.76	62.32	64.37
Viscosity Index	112.6	114.5	135.1	140.3	150.8	150.2

Table 53

PARATONE

Sample No.	76	77	78	79	80	81
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-
Per cent Wax added	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	25	20	20	15	20	25
Cloud Point (°F)	42	44	44	40	46	44
Viscosities						
Centistokes						
100°	26.48	28.0	34.28	39.69	54.38	79.27
130°	-	-	-	-	-	-
210°	4.17	5.02	6.05	6.93	9.05	12.88
Saybolt Univ. Seconds						
100°	125.4	132.1	159.9	184.4	251.5	366.3
210°	41.56	42.66	45.98	48.82	55.96	69.64
Viscosity Index	111	117.8	130.8	136.1	138	141

Table54

VINYL ETHER RESIN

Sample No.	364	365	366	367	368	369
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin	-	-	-	-	-
Per cent Wax added	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	20	15	-	10	-
Viscosities						
Centistokes						
100°	-	25.55	28.16	-	40.2	-
130°	-	-	-	-	-	-
210°	-	4.61	5.04	-	7.06	-
Saybolt Univ. Seconds						
100°	-	121.3	132.8	-	186.6	-
210°	-	41.33	42.73	-	49.24	-
Viscosity Index	-	105.8	117.9	-	137.4	-

Table 55

SANTOFOUR B

Sample No.	262	263	264	265	266	267
Base Oil	White Oil	-	-	-	-	-
Wax	Microcrystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-10	-15	-	-30	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	25.3	26.0	-	27.0	-
130°	-	13.91	14.24	-	14.86	-
210°	-	4.54	4.65	-	4.80	-
Saybolt Univ. Seconds						
100°	-	120.2	123.3	-	127.7	-
210°	-	41.11	41.46	-	41.95	-
Viscosity Index	-	101.3	104.9	-	109.0	-

Table 56

POUREX

Sample No.	208	209	210	211	212	213
Base Oil	White Oil	-	-	-	-	-
Wax	Microcrystalline		-	-	-	-
Per cent Wax added	-	-	-	-	-	-
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-20	-10	-	-25	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	25.5	26.8	-	28.4	-
130°	-	13.94	14.33	-	15.15	-
210°	-	4.55	4.69	-	4.88	-
Saybolt Univ. Seconds						
100°	-	121.1	126.8	-	133.9	-
200°	-	41.14	41.60	-	42.21	-
Viscosity Index	-	100.3	102.8	-	103.8	-

Table 57

SANTOPOUR C

Sample No.	196	197	198	199	200	201
Base Oil	White Oil	-	-	-	-	-
Wax	Microcrystalline		-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-20	-20	-	-30	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	26.5	29.3	-	42.3	-
130°	-	14.62	16.4	-	24.26	-
210°	-	4.78	5.45	-	8.13	-
Saybolt Univ. Seconds						
100°	-	125.5	137.8	-	196.0	-
210°	-	41.89	44.05	-	52.8	-
Viscosity Index	-	112.0	133.1	-	149.2	-

Table 58

PARAFLOW 46X

Sample No.	45	46	47	48	49	50
Base Oil	White Oil C	-	-	-	-	-
Wax	Microcryst-alline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour °F	+5	+5	0	-20	-10	+5
Cloud °F	Rm. Temp.	-	-	-	-	-
Viscosity °F						
Centistokes						
100°	29.8	30.[illegible]	30.8	33.0	36.0	36.6
130°	15.1	15.3	15.9	16.93	18.19	19.01
210°	4.64	4.67	4.81	5.00	5.39	5.7
Saybolt Univ. Seconds						
100°	140.9	140.9	144.4	154.2	167.7	170.4
130°						
210°	41.43	41.54	41.7	42.3	43.86	44.93
Viscosity Index	64.3	66.8	75.44	76.6	88.6	105.7

Table 59

SANTOPOUR

Sample No.	64	65	66	67	68	69
Base Oil	White Oil C	-	-	-	-	-
Wax	Microcryst-alline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour °F	-10°	-15°	-15°	-20°	-10°	0°
Cloud °F	-	-	-	-	-	-
Viscosity °F						
Centistokes						
100°	27.5	28.0	27.8	28.4	29.8	31.0
130°	14.72	14.93	14.88	15.10	15.65	16.29
210°	4.61	4.65	4.72	4.75	4.90	4.06
Saybolt Univ. Seconds						
100°	129.9	132.1	131.2	133.9	140.0	145.3
130°						
210°	41.33	41.46	41.69	41.79	42.28	42.79
Viscosity Index	84.9	84.5	93.76	91.2	92.9	97.5

Table 60

PARAFLOW PDX

Sample No.	100	101	102	103	104	105
Base Oil	White Oil	-	-	-	-	-
Wax	Micro-Crystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-10	-15	-20	-20	-15	-15
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	27.4	28.0	29.9	31.9	33.8	36.0
130°	14.5	14.78	15.49	16.2	17.4	18.69
210°	4.59	4.62	4.75	4.87	5.29	5.61
Saybolt Univ. Seconds						
100°	129.5	132.1	140.5	149.3	157.8	167.7
210°	40.27	41.37	41.79	42.18	43.54	44.56
Viscosity Index	84.05	80.95	76.9	72.0	95.4	102.7

Table 61

ACRYLOID 710

Sample No.	118	119	120	121	122	123
Base Oil	White Oil	-	-	-	-	-
Wax	Micro Crystalline		-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (^{o}F)	+10	+5	-10	-5	-10	-10
Cloud Point (^{o}F)	-	---	-	-	0	-
Viscosities						
Centistokes						
100^{o}	28.6	30.0	35.6	40.4	57.0	78.0
130^{o}	15.13	16.03	19.37	22.58	32.63	45.01
210^{o}	4.81	5.11	6.21	7.49	10.92	15.2
Saybolt Univ. Seconds						
100^{o}	134.7	140.9	165.9	187.5	263.6	360.4
210^{o}	41.98	42.95	46.49	50.67	62.46	78.53
Viscosity Index	95.25	108.9	130.5	144.3	150.6	150.6

Table 62

SANTOLUBE 203-A

Sample No.	298	299	300	301	302	303
Base Oil	White Oil	-	-	-	-	-
Wax	Microcrystalline		-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-5	-5	-	0	-
Viscosities						
Centistokes						
100°	-	25.3	26.0	-	27.0	-
130°	-	13.89	14.14	-	14.86	-
210°	-	4.55	4.66	-	4.82	-
Saybolt Univ. Seconds						
100°	-	120.2	123.3	-	127.7	-
210°	-q	41.14	41.50	-	42.02	-
Viscosity Index	-	102.4	106.0	-	110.8	-

Table 63

ACRYLOID 150

Sample No.	19	20	21	22	23	24	25
Base Oil	White Oil C*	-	-	-	-	-	-
Wax	Microcrystalline	-	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0	0.5	1.0	3.0	5.0	10.0	15.0
Pour °F	+15°	+5°	-5°	0°	0°	+5°	+5°
Cloud°F	Rm. Temp.	-	-	-	-	-	-
Viscosity°F							
Centistokes							
100°	33.7	42.02	42.89	50.55	66.24	93.77	124.0
130°	14.67	-	-	-	-	-	-
210°	4.59	5.07	5.75	6.6	8.46	13.18	16.93
S.U.S.							
100°	158.0	194.8	198.7	233.9	306.1	433.2	572.88
130°							
210°	41.1	42.82	45.02	47.75	53.94	70.81	85.42
Viscosity Index	8.0	14.45	75.02	87.4	106.3	131.2	132.7

Table 64

SANTODEX

Sample No.	172	173	174	175	176	177
Base Oil	White Oil	-	-	-	-	-
Wax	Micro-crystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	10	10	-	5	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	28.9	31.5	-	52.5	-
130°	-	15.0	17.23	-	28.35	-
210°	-	4.87	5.71	-	9.36	-
Saybolt Univ. Seconds						
100°	-	136.1	147.5	-	242.9	-
210°	-	42.18	44.88	-	57.02	-
Viscosity Index	-	98.25	131.8	-	144.5	-

Table 65

ACRYLOID HF 600

Sample No.	154	155	156	157	158	159
Base Oil	White Oil	-	-	-	-	-
Wax	Microcrystalline-		-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	10	5	-	10	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	27.8	31.2	-	-	47.6	-
130°	15.38	17.31	-	-	28.49	-
210°	5.12	5.83	-	-	10.23	-
Saybolt Univ. Seconds						
100°	131.2	146.2	-	-	220.4	-
210°	42.68	45.28	-	-	60.02	-
Viscosity Index	125.8	137.8	-	-	158.0	-

Table 66

LOW MOLECULAR WEIGHT POLYBUTENE

Sample No.	226	227	228	229	230	231
Base Oil	White Oil	-	-	-	-	-
Wax	Microcrystalline		-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	10	10	-	10	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	32.1	33.9	-	54.0	-
130°	-	17.53	18.27	-	29.56	-
210°	-	5.61	5.85	-	9.20	-
Saybolt Univ. Seconds						
100°	-	150.2	158.2	-	249.9	-
210°	-	44.56	45.34	-	56.41	-
Viscosity Index	-	124.3	125.2	-	140.4	-

Table 67

HIGH MOLECULAR WEIGHT POLYBUTENE

Sample No.	244	245	246	247	248	249
Base Oil	White Oil	-	-	-	-	-
Wax	Microcrystalline		-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	10	10	-	5	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	29.0	32.2	-	53.5	-
130°	-	15.51	17.64	-	29.01	-
210°	-	4.98	5.65	-	8.87	-
Saybolt Univ. Seconds						
100°	-	136.5	150.6	-	247.5	-
210°	-	42.54	44.69	-	55.34	-
Viscosity Index	-	106.7	125.5	-	154.7	-

Table 68

ACRYLOID 722

Sample No.	136	137	138	139	140	141
Base Oil	White Oil	-	-	-	-	-
Wax	Microcrystalline		-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	15	15	15	10	10	10
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	28.6	29.4	33.9	37.2	48	68.64
130°	15.13	15.5	18.23	20.47	27.75	35.85
210°	4.87	4.95	5.92	6.73	9.27	11.9
Saybolt Univ. Seconds						
100°	134.7	138.3	158.2	173.1	222.2	295.8
210°	42.18	42.44	45.56	48.17	56.72	66.0
Viscosity Index	99.96	100.9	127.8	139.3	150.7	148.7

Table 69

PARATONE

Sample No.	82	83	84	85	86	87
Base Oil	White Oil	-	-	-	-	-
Wax	Micro-crystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	5	5	10	10	10	10
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	28.8	31.0	34.1	39.8	55	70.5
130°	15.41	16.39	18.14	21.21	29.68	39.25
210°	4.88	5.19	6.72	6.64	9.09	11.86
Saybolt Univ. Seconds						
100°	135.6	145.3	159.2	184.8	254.4	325.7
210°	42.21	43.21	44.92	47.88	56.1	65.86
Viscosity Index	99.96	107.3	118.5	128.3	137.5	142.9

Table 70

VINYL ETHER RESIN

Sample No.	376	377	378	379	380	381
Base Oil	White Oil	-	-	-	-	-
Wax	Microcrystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	15	15	-	15	-
Viscosities						
Centistokes						
100°	-	26.0	28.0	-	38.9	-
130°	-	14.23	15.62	-	21.74	-
210°	-	4.70	5.15	-	7.02	-
Sayvolt Univ. Seconds						
100°	-	123.3	132.1	-	180.8	-
210°	-	41.63	43.08	-	49.11	-
Viscosity Index	-	109.7	126.1	-	140.6	-

Table 71

SANTOPOUR B

Sample No.	268	269	270	271	272	273
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin and Microcrystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-30	-40	-	-40	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	24.8	25.2	-	26.8	-
130°	-	13.5	13.78	-	14.46	-
210°	-	4.44	4.56	-	4.71	-
Saybolt Univ. Seconds						
100°	-	118.0	119.8		126.8	-
210°	-	40.79	41.17		41.66	-
Viscosity Index	-	96.16	104.6	-	102.9	-

Table 72

PARAFLOW PDX

Sample No.	106	107	108	109	110	111
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin and Microcrystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-15	-10	-15	-15	-35	-35
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	26.6	27.2	28.0	29.4	31.8	36.1
130°	14.21	14.44	14.88	15.55	16.69	18.48
210°	4.52	4.59	4.68	4.85	5.21	5.52
Saybolt Univ. Seconds						
100°	126.0	128.6	132.1	138.3	148.8	168.2
210°	41.04	41.27	41.56	42.12	43.27	44.27
Viscosity Index	84.6	86.1	87.8	91.9	103.2	96.8

Table 73

SANTOPOUR C

Sample No.	190	191	192	193	194	195
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin and Microcrystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-15	-10	-	-20	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	27.2	30	-	43.4	-
130°	-	14.78	16.56	-	24.6	-
210°	-	4.82	5.46	-	8.23	-
Saybolt Univ. Seconds						
100°	-	128.6	140.9	-	201.0	-
210°	-	42.02	44.08	-	53.15	-
Viscosity Index	-	109.0	129.4	-	148.2	-

Table 74

SANTOPOUR

Sample No.	70	71	72	73	74	75
Base Oil	White Oil C	-	-	-	-	-
Wax	Paraffin and Microcrystalline		-	--	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour (°F)	0	-15	-25	-20	-15	-20
Cloud (°F)	-	-	--	-	-	-
Viscosity °F						
Centistokes						
100°	29.8	29.9	30.0	30.0	30.0	31.9
130°	15.16	15.20	15.21	15.25	15.75	16.58
210?	4.59	4.60	4.65	4.72	4.89	5.12
Saybolt Univ. Seconds						
100°	140.0	140.5	140.9	140.9	140.9	149.3
130°	-	-	-	-	-	-
210?	41.27	41.3	41.46	41.69	42.25	42.98
Viscosity Index	58.08	58.3	63.9	72.45	90.7	95.7

Table 75

POUREX

Sample No.	214	215	216	217	218	219
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin and Microcrystalline	-	-	-	-	-
Per cent Wax added	2.0	2.0	2.0	2.0	2.0	2.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-20	-20	-	-25	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	25.3	26.1	-	27.5	-
130°	-	13.72	14.06	-	14.16	-
210°	-	4.5	4.63	-	4.81	-
Saybolt Univ. Seconds						
100°	-	120.2	123.7	-	129.9	-
210°	-	40.98	41.4	-	41.98	-
Viscosity Index	-	97.0	102.0	-	105.3	-

Table 75

PARAFLOW 46X

Sample No.	51	52	53	54	55	56
Base Oil	White Oil C	-	-	-	-	-
Wax	Paraffin and Microcrystalline		-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour °F	+10	+5	0	-10	-20	0
Cloud °F	Rm. Temp.	-	-	-	-	-
Viscosity °F						
Centistokes						
100°	29.8	30.1	30.2	32.3	34.3	37.2
130°	15.11	15.32	15.79	16.46	17.71	19.01
210°	4.6	4.64	4.77	4.96	5.35	5.71
Saybolt Univ. Seconds						
100°	140.0	141.3	141.8	151.0	158.7	173.1
130°	-	-	-	-	-	-
210°	41.31	41.43	41.56	42.47	43.73	44.88
Viscosity Index	59.9	61.5	76.4	78.04	98.32	101.9

Table 77

SANTOLUBE 203-A

Sample No.	304	305	306	307	308	309
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin and Microcrystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-		-	-
Cloud Point (°F)	-	-10	-15	-	-5	-
Viscosities						
Centistokes						
100°	-	24.7	25.0	-	26.3	-
130°	-	13.48	13.74	-	14.51	-
210°	-	4.41	4.57	-	4.8	-
Saybolt Univ. Seconds						
100°	-	117.6	118.9	-	124.6	-
210°	-	40.88	41.25	-	41.95	-
Viscosity Index	-	100.7	107.8	-	115.5	-

Table 78

ACRYLOID 150

Sample No.	26	27	28	29	30	31	32
Base Oil	White Oil C	-	-	-	-	-	-
Wax	Paraffin and Microcrystalline		-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0	0.5	1.0	3.0	5.0	10.0	15.0
Pour °F	+15°	-5°	-10°	-10°	-15°	-15°	15°
Cloud °F	Rm. Temp.	-	-	-	-	-	-
Viscosity °F							
Centistokes							
100°	28.44	31.55	31.89	38.31	48.5	77.0	119.7
130°	13.73	-	-	-	-	-	-
210°	4.5	4.88	5.07	6.38	8.11	12.5	17.39
Saybolt Univ. Seconds							
100°	134.1	147.7	149.3	182.6	222.5	337.0	520.0
130°	-	-	-	-	-	-	-
210°	40.98	42.21	42.82	47.05	52.74	67.9	86.0
Viscosity Index	61.45	75.23	91.4	120.6	135.5	140.0	140.0

Table 79

ACRYLOID 710

Sample No.	124	125	126	127	128	129
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin and Microcrystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	+15	5	5	5	5	5
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	28.1	30.3	34.1	39.8	59.5	92.5
130°	15.04	16.3	18.88	22.05	32.94	53.91
210°	4.79	5.3	6.24	7.28	11.04	18.41
Saybolt Univ. Seconds						
100°	132.5	142.2	159.2	184.8	275.1	427.4
210°	41.92	43.57	46.59	49.97	62.88	91.51
Viscosity Index	97.89	119.1	137.7	142.3	148.5	150.1

Table 80

SANTODEX

Sample No.	178	179	180	181	182	183
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin and Microcrystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	10	10	-	10	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	27.4	32.0	-	49.0	-
130°	-	14.79	17.2	-	27.8	-
210°	-	4.76	5.61	-	9.22	-
Saybolt Univ. Seconds						
100°	-	129.5	149.7	-	226.8	-
210°	-	41.82	44.56	-	56.54	-
Viscosity Index	-	101.7	124.8	-	148.7	-

Table 81

ACRYLOID HF 600

Sample No.	160	161	162	163	164	165
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin and Microcrystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	51.0	10.0	15.0
Pour Point (°F)	-	10	10	-	5	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	26.8	31.0	-	44.8	-
130°	-	14.89	17.22	-	27.65	-
210°	-	4.94	5.88	-	10.17	-
Saybolt Univ. Seconds						
100°	-	126.8	145.3	-	207.5	-
210?	-	42.41	45.44	-	59.81	-
Viscosity Index	-	121.8	140.4	-	161.3	-

Table 82

HIGH MOLECULAR WEIGHT POLYBUTENE

Sample No.	250	251	252	253	254	255
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin and Microcrystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	10	10	-	10	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	27.0	31.0	-	52.4	-
130°	-	14.8	17.02	-	28.65	-
210°	-	4.8	5.51	-	8.83	-
Saybolt Univ. Seconds						
100°	-	127.7	145.3	-	242.9	-
210°	-	41.95	44.24	-	52.2	-
Viscosity Index	-	109.0	125.8	-	138.4	-

Table 83

LOW MOLECULAR WEIGHT POLYBUTENE

Sample No.	232	233	234	235	236	237
Base Oil	White Oil	-	-	-	-	--
Wax	Paraffin and Microcrystalline		-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	10	5	-	10	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	28.7	32.2	-	52.7	-
130°	-	15.06	17.74	-	28.73	-
210°	-	4.90	5.73	-	8.99	-
Saybolt Univ. Seconds						
100°	-	135.2	150.6	-	243.8	-
210°	-	42.28	44.95	-	55.76	-
Viscosity Index	-	111.1	128.9	-	140.1	-

Table 84

ACRYLOID 722

Sample No.	142	143	144	145	146	147
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin and Microcrystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	15	10	15	20	20	15
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	27.4	29.0	33.2	39.6	51.8	63.0
130°	14.79	15.63	18.03	21.48	28.2	35.57
210°	4.79	5.01	5.87	6.95	9.29	11.89
Saybolt Univ. Seconds						
100°	129.5	136.5	155.1	183.9	239.7	291.2
210°	41.92	42.63	45.4	48.88	56.78	65.97
Viscosity Index	104.8	109.4	129.3	136.9	146.5	149.7

Table 85

PARATONE

Sample No.	88	89	90	91	92	93
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin & Micro-crystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	20	20	20	15	20	20
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	27.7	28.5	34.5	37.0	53	83.0
130°	14.9	15.21	18.6	19.78	29.16	44.95
210°	4.75	4.9	5.87	6.21	9.06	13.51
Saybolt Univ. Seconds						
100°	130.8	134.3	161.0	172.2	245.2	383.5
210°	41.79	42.28	45.4	46.49	55.99	72.04
Viscosity Index	97.9	104.3	123.6	124.7	140.5	141.2

Table 86

VINYL ETHER RESIN

Sample No.	370	371	372	373	374	375
Base Oil	White Oil	-	-	-	-	-
Wax	Paraffin and Nicrocrystalline	-	-	-	-	-
Per cent Wax added	1.0	1.0	1.0	1.0	1.0	1.0
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	10	15	-	15	-
Viscosities Centistokes						
100°	-	26.1	29.3	-	40.0	-
130°	-	14.37	15.82	-	21.96	-
210°	-	4.70	5.15	-	7.04	-
Saybolt Univ. Seconds						
100°	-	123.7	137.8	-	185.7	-
210°	-	41.63	43.08	-	49.17	-
Viscosity Index	-	108.7	116.7	-	132.6	-

Table 87

	Paraflow PDX				Acryloid 710		
Sample No.	407	408	409	410	413	414	416
Base Oil	Penn Bright Stock				Penn Bright Stock		
Per cent Additive	1.0	3.0	5.0	10.0	1.0	3.0	5.0
Pour Point (°F)	0	-10	-10	-10	0	0	0
Viscosities Centistokes							
100°	470.5	466.3	460.8	445.4	483.6	477.4	641.5
130°	-	-	-	-	-	-	-
210°	31.2	31.07	30.86	30.50	32.5	32.66	50.43
Saybolt Univ. Seconds							
100°	2173.7	2154.3	2128.9	2063.4	2234.2	2205.6	2963.7
210°	147.2	146.6	145.7	144.1	153.0	153.7	235.0
Viscosity Index	102.4	102.5	102.7	103.6	104.5	106.0	118.8

Table 88

	Santopour				Paratone		
Sample No.	395	396	397	398	401	402	404
Base Oil	Penn Bright Stock				Penn Bright Stock		
Per cent Additive	1.0	3.0	5.0	10.0	1.0	3.0	10.0
Pour Point(°F)	+5	-10	-10	-10	+10	+10	+10
Viscosities Centistokes							
100°	468.3	447.4	425.4	380.7	496.9	534.2	707.7
130°	-	-	-	-	-	-	-
210°	31.06	30.12	29.28	27.15	32.61	35.7	48.54
Saybolt Univ. Seconds							
100°	2163.5	2067.0	1965.3	1758.8	2295.7	2468.0	3269.6
210°	146.6	142.4	138.7	129.3	153.2	106.7	113.8
Viscosity Index	102.3	102.3	102.9	102.8	103.2	106.7	113.8

Table 89

	Santodex			Santopour C		
Sample No.	431	432	434	437	438	440
Base Oil	Penn Bright Stock			Penn Bright Stock		
Per cent Additive	1.0	3.0	10.0	1.0	3.0	10.0
Pour Point (°F)	+10	+10	+10	-5	-10	-5
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	477.3	486.0	536.9	486.6	508.7	584.3
130°	-	-	-	-	-	-
210°	31.98	34.06	42.2	32.53	34.66	42.17
Saybolt Univ. Seconds						
100°	2205.1	2245.3	2480.5	2248.1	2350.2	2699.5
130°	-	-	-	-	-	-
210°	150.7	160.1	197.0	153.1	162.8	196.8
Viscosity Index	103.8	108.1	117.9	104.2	107.0	113.9

Table 90

	Acryloid 150			Paraflow 46X		
Sample No.	383	384	386	389	390	392
Base Oil	Penn Bright Stock			Penn Bright Stock		
Per cent Additive	1.0	3.0	10.0	1.0	3.0	10.0
Pour Point (°F)	-5	-5	-5	+5	+5	+5
Viscosities Centistokes						
100°	496.4	505.4	572.3	476.1	469.2	450.8
130°	-	-	-	-	-	-
210°	32.96	33.67	39.33	31.4	31.21	30.95
Saybolt Univ. Seconds						
100°	2293.4	2334.9	2644.0	2199.6	2167.7	2082.7
130°	-	-	-	-	-	-
210°	155.1	158.3	183.9	148.1	147.2	146.1
Viscosity Index	104.2	105.0	110.3	102.3	102.6	104.3

Table 91

	Santolube 203A			Vinyl Ether Resin		
Sample No.	473	474	476	497	498	500
Base Oil	Penn Bright Stock			Penn Bright Stock		
Per cent Additive	1.0	3.0	10.0	1.0	3.0	10.0
Pour Point (°F)	+10	0	-10	+10	+10	+10
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	471.5	455.9	401.6	473.8	474.3	470.4
130°	-	-	-	-	-	-
210°	31.16	30.43	28.16	31.6	32.36	35.11
Saybolt Univ. Seconds						
100°	2178.3	2106.3	1855.4	2189.0	2191.3	2173.2
130°	-	-	-	-	-	-
210°	147.0	148.8	133.7	149.0	152.4	164.8
Viscosity Index	102.2	102.1	102.8	103.2	105.3	112.0

Table 92

	Pourex			Low Molecular Weight Polybutene		
Sample No.	443	444	446	449	450	452
Base Oil	Penn Bright Stock			Penn Bright Stock		
Per cent Additive	1.0	3.0	10.0	1.0	3.0	10.0
Pour Point (°F)	+10	0	-5	+10	+10	+10
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	469.4	450.3	394.4	495.6	532.7	689.9
130°	-	-	-	-	-	-
210°	31.15	30.30	27.63	32.77	35.47	47.29
Saybolt Univ. Seconds						
100°	2168.6	2080.4	1822.1	2289.7	2461.1	3187.2
130°	-	-	-	-	-	-
210°	147.0	143.2	131.4	154.4	166.5	220.5
Viscosity Index	102.4	102.5	102.1	103.8	106.4	113.4

Table 93

	High Molecular Weight Polybutene			Santopour B		
Sample No.	455	456	458	461	462	464
Base Oil	Penn Bright Stock			Penn Bright Stock		
Per cent Additive	1.0	3.0	10.0	1.0	3.0	10.0
Pour Point (°F)	+10	+10	+10	+5	+5	-10
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	501.3	543.1	702.3	465.7	447.5	378.1
130°	-	-	-	-	-	-
210°	32.94	35.72	46.36	30.94	30.09	27.14
Saybolt Univ. Seconds						
100°	2316.0	2509.1	3244.6	2151.5	2067.4	1746.8
130°	-	-	-	-	-	-
210°	155.0	167.6	116.1	146.1	142.3	129.2
Viscosity Index	103.7	105.9	111.5	102.3	102.2	103.2

Table 94

	Acryloid 722			Acryloid HF-600		
Sample No.	419	420	422	425	426	428
Base Oil	Penn Bright Stock			Penn Bright Stock		
Per cent Additive	1.0	3.0	10.0	1.0	3.0	10.0
Pour Point (°F)	-10	0	-10	+10	+5	+10
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	470.1	460.6	554.5	463.6	440.6	843.5
130°	-	-	-	-	-	-
210°	31.22	31.13	42.7	31.03	33.54	74.77
Saybolt Univ. Seconds						
100°	2171.9	2128.0	2561.8	2141.8	2035.6	3897.0
130°	-	-	-	-	-	-
210°	147.3	146.9	199.5	146.4	157.8	347.8
Viscosity Index	102.6	103.5	116.5	102.8	112.1	123.7

Table 95

ACRYLOID 150

Sample No.	700	701	702	703	704	705
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-10	-10	-	+10	-
Cloud Point (°F)	-	+14	+12	-	+14	-
Viscosities Centistokes						
100°	-	596.8	595.2	-	-	-
210°	-	37.2	36.89	-	-	-
Saybolt Univ. Seconds						
100°	-	2757.2	2749.8	-	-	-
210°	-	174.3	173.0	-	-	-
Viscosity Index	-	104.0	106.0	-	114.0	-

Table 96

SANTOPOUR B

Sample No.	777	778	779	780	781	782
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-5	0	-	-10	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 97

SANTOPOUR C

Sample No.	754	755	756	757	758	759
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	0.5	1.0	-	5.0	-	-
Pour Point (°F)	0	-5	-	-10	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	539.4	550.7	-	611.8	-	-
130°	-	-	-	-	-	-
210°	32.77	34.49	-	42.57	-	-
Saybolt Univ. Seconds						
100°	2492.0	2544.2	-	2826.5	-	-
130	-	-	-	-	-	-
210°	154.2	162.1	-	198.6	-	-
Viscosity Index	98.51	102.0	-	112.2	-	-

Table 98

SANTOPOUR

Sample No.	712	713	714	715	716	717
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	0	0	-	-10	-
Cloud Point	-	+16	+18	-	+28	-
Viscosities Centistokes						
100°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 99

PARAFLOW 46X

Sample No.	706	707	708	709	710	711
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	0	0	-	0	-
Cloud Point (°F)	-	+10	+12	-	+12	-
Viscosities Centistokes						
100°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 100

SANTOLUBE 203A

Sample No.	783	784	785	786	787	788
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	0	0	-	0	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 101

POUREX

Sample No.	760	761	762	763	764	765
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	+5	0	-	-10	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	-	519.0	502.6	-	437.7	-
130°	-	-	-	-	-	-
210°	-	31.28	30.72	-	28.04	-
Saybolt Univ. Seconds						
100°	-	2397.8	2368.2	-	2022.2	-
130°	-	-	-	-	-	-
210°	-	147.6	145.1	-	133.2	-
Viscosity Index	-	96.27	96.57	-	96.39	-

Table 102

PARAFLOW PDX

Sample No.	724	725	726	727	728	729
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	+10	0	-	-10	-
Cloud Point (°F)	-	+20	+20	-	+20	-
Viscosities Centistokes						
100°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 103

PARATONE

Sample No.	718	719	720	721	722	723
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	-	541.5	594.7	-	797.9	-
210°	-	32.35	36.31	-	50.48	-
Saybolt Univ. Seconds						
100°	-	2501.7	2747.5	-	3686.3	-
210°	-	152.3	170.2	-	235.3	-
Viscosity Index	-	96.9	102.1	-	111.3	-

Table 104

30% VINYL ETHER RESIN IN OIL

Sample No.	789	790	791	792	793	794
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	-	530.8	526.4	-	527.5	-
210°	-	32.17	32.83	-	35.67	-
Saybolt Univ. Seconds						
100°	-	2452.3	2432.0	-	2437.0	-
210°	-	151.6	154.5	-	167.4	-
Viscosity Index	-	97.63	100.2	-	107.3	-

Table 105

ACRYLOID 710

Sample No.	730	731	732	733	734	735
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	-	537.1	556.2	-	654.1	-
130°	-	-	-	-	-	-
210°	-	33.26	36.4	-	50.65	-
Saybolt Univ. Seconds						
100°	-	2481.4	2569.6	-	3021.9	-
130°	-	-	-	-	-	-
210°	-	156.4	170.7	-	236.0	-
Viscosity Index	-	100.2	106.1	-	118.4	-

Table 106

ACRYLOID 722

Sample No.	736	737	738	739	740	741
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	-	540.0	532.3	-	646.8	-
130°	-	-	-	-	-	-
210°		33.29	31.78		47.01	
Saybolt Univ. Seconds						
100°	-	2494.8	2459.2	-	2988.2	-
130°	-	-	-	-	-	-
210°	-	156.6	149.8	-	219.1	-
Viscosity Index	-	100	106.2	-	115.5	-

Table 107

ACRYLOID HF 600

Sample No.	742	743	744	745	746	747
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	-	563.1	629.9	-	743.0	-
130°	-	-	-	-	-	-
210°	-	35.15	42.95	-	58.14	-
Saybolt Univ. Seconds						
100°	-	2476.8	2910.1	-	3432.7	-
130°	-	-	-	-	-	-
210°	-	165.0	200.3	-	270.7	-
Viscosity Index	-	102.4	111.5	-	119.9	-

Table 108

SANTODEX

Sample No.	748	749	750	751	752	753
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	-	535.3	546.9	-	613.5	-
130°	-	-	-	-	-	-
210°	-	32.8	34.88	-	44.97	-
Saybolt Univ. Seconds						
100°	-	2413.1	2526.7	-	2834.4	-
130°	-	-	-	-	-	-
210°	-	154.4	163.8	-	209.8	-
Viscosity Index	-	99.09	103.3	-	115.3	-

Table 109

HIGH MOLECULAR WEIGHT POLYBUTENE

Sample No.	771	772	773	774	775	776
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	-	561.1	608.4	-	745.4	-
210°	-	33.49	36.4	-	45.03	-
Saybolt Univ. Seconds						
100°	-	2592.3	2810.8	-	3443.7	-
210°	-	157.6	170.7	-	210.0	-
Viscosity Index	-	98.13	101.0	-	107	-

Table 110

LOW MOLECULAR WEIGHT POLYBUTENE

Sample No.	765	766	767	768	769	770
Base Oil	Mid-Continent Bright Stock					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	-	552.8	597.9	-	776.6	-
210°	-	33.16	36.21	-	48.68	-
Saybolt Univ. Seconds						
100°	-	2553.9	2763.3	-	3587.9	-
210°	-	156.0	169.8	-	226.9	-
Viscosity Index	-	98.09	101.6	-	110.3	-

Table 111

ACRYLOID 150

Sample No.	502	503	504	505	506	507
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	-
Pour Point (°F)	-40	-40	-40	-	-35	-
Cloud Point (°F) for 150 vis	10	12	12	-	14	-
Viscosities Centistokes						
100°	34.38	36.52	46.09	-	92.06	-
130°	-	-	-	-	-	-
210°	5.52	5.84	7.44	-	14.94	-
Saybolt Univ. Seconds						
100°	160.4	170.1	213.5	-	425.3	-
130°	-	-	-	-	-	-
210°	44.27	45.31	50.50	-	77.51	-
Viscosity Index	106.7	111.9	128.5	-	141.5	-

Table 112

PARAFLOW PDX

Sample No.	526	527	528	529	530	531
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-35	-45	-50	-50	-
Cloud Point (°F)	-	12	12	12	10	-
Viscosities Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 113

SANTOPOUR C

Sample No.	556	557	558	559	560	561
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-35	-35	-	-25	-
Cloud Point (°F)	-	10	14	-	16	-
Viscosities Centistokes						
100°	-	33.97	38.41	-	57.42	-
130°	-	-	-	-	-	-
210°	-	5.45	6.14	-	9.12	-
Saybolt Univ. Seconds						
100°	-	160.4	178.5	-	265.5	-
130°	-	-	-	-	-	-
210°	-	44.05	46.27	-	56.20	-
Viscosity Index	-	105.0	116.0	-	130.5	-

Table 114

PARAFLOW 46X

Sample No.	508	509	510	511	512	513
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-30	-40	-	-10	-
Cloud Point (°F)	-	16	+10	-	+10	-
Viscosities Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 115

SANTOPOUR B

Sample No.	580	581	582	583	584	585
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-30	-40	-	-45	-
Cloud Point(°F)	-	10	10	-	12	-
Viscosities Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 116

SANTOPOUR

Sample No.	514	515	516	517	518	519
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-30	-40	-25	0	-
Cloud Point (°F)	-	12	12	12	10	-
Viscosities Centistokes						
100°	-	32.38	32.76	-	33.54	-
130°	-	-	-	-	-	-
210°	-	5.16	5.22	-	5.30	-
Saybolt Univ. Seconds						
100°	-	151.4	153.1	-	156.6	-
130°	-	-	-	-	-	-
210°	-	43.11	43.31	-	43.57	-
Viscosity Index	-	95.3	97.3	-	97.8	-

Table 117

POUREX

Sample No.	562	563	564	565	566	567
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-10	-30	-	-40	-
Cloud Point (°F)	-	+12	+16	-	+18	-
Viscosities Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 118

ACRYLOID 722

Sample No.	538	539	540	541	542	543
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	0.5	1.0	3.0	-	10.0	15.0
Pour Point (°F)	-	0	-25	-	-40	-
Cloud Point (°F)	-	14	16	-	14	-
Viscosities Centistokes						
100°	-	34.68	40.36	-	65.98	-
130°	-	-	-	-	-	-
210°	-	5.60	6.56	-	10.99	-
Saybolt Univ. Seconds						
100°	-	161.7	187.3	-	304.9	-
130°	-	-	-	-	-	-
210°	-	44.53	47.62	-	62.70	-
Viscosity Index	-	109.5	123.1	-	140.8	-

Table 119

SANTOLUBE 203A

Sample No.	592	593	594	595	596	597
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-5	-20	-	-25	-
Cloud Point (°F)	-	+12	+12	-	+12	-
Viscosities Centistokes						
100°	-	32.35	32.82	-	34.62	-
130°	-	-	-	-	-	-
210°	-	5.16	5.22	-	5.40	-
Saybolt Univ. Seconds						
100°	-	151.3	153.4	-	161.5	-
130°	-	-	-	-	-	-
210°	-	43.11	43.31	-	43.89	-
Viscosity Index	-	95.56	96.9	-	97.8	-

Table 120

HIGH MOLECULAR WEIGHT POLYBUTENE

Sample No.	574	575	576	577	578	579
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	-	34.82	41.08	-	70.20	-
130°	-	-	-	-	-	-
210°	-	5.52	6.37	-	10.18	-
Saybolt Univ. Seconds						
100°	-	162.4	190.5	-	324.3	-
130°	-	-	-	-	-	-
210°	-	44.27	47.01	-	59.85	-
Viscosity Index	-	104.2	113.8	-	128.0	-

Table 121

LOW MOLECULAR WEIGHT POLYBUTENE

Sample No.	568	569	570	571	572	573
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	-	34.77	40.66	-	67.95	-
130°	-	-	-	-	-	-
210°	-	5.22	6.36	-	10.15	-
Saybolt Univ. Seconds						
100°	-	162.1	188.6	-	314.0	-
130°	-	-	-	-	-	-
210°	-	44.27	46.98	-	59.74	-
Viscosity Index	-	104.5	115.1	-	130.6	-

Table 122

SANTODEX

Sample No.	550	551	552	553	554	555
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	-	34.51	39.67	-	62.90	-
130°	-	-	-	-	-	-
210°	-	5.53	6.38	-	10.15	-
Saybolt Univ. Seconds						
100°	-	161.0	184.3	-	290.7	-
130°	-	-	-	-	-	-
210°	-	44.31	47.05	-	59.74	-
Viscosity Index	-	106.6	119.7	-	137.3	-

Table 123

PARATONE

Sample No.	520	521	522	523	524	525
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	35.08	41.72	-	72.41	-
130°	-	-	-	-	-	-
210°	-	5.57	6.51	-	10.76	-
Saybolt Univ. Seconds						
100°	-	163.5	193.5	-	331.5	-
130°	-	-	-	-	-	-
210°	-	44.13	47.46	-	61.89	-
Viscosity Index	-	105.5	116.4	-	131.5	-

Table 124

ANALYSIS 710

Sample No.	532	533	534	535	536	537
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	15	0	-	0	-
Cloud Point (°F)	-	12	12	-	14	-
Viscosities						
Centistokes						
100°	-	35.43	43.02	-	77.99	-
130°	-	-	-	-	-	-
210°	-	5.73	7.06	-	13.32	-
Saybolt Univ. Seconds						
100°	-	165.1	199.3	-	360.4	-
130°	-	-	-	-	-	-
210°	-	44.95	49.24	-	71.32	-
Viscosity Index	-	112.1	128.8	-	144.0	-

Table 125

ACRYLOID HF 600

Sample No.	544	545	546	547	548	549
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	+5	+5	-	+5	-
Cloud Point (°F)	-	14	16	-	14	-
Viscosities Centistokes						
100°	-	38.03	50.14	-	122.5	-
130°	-	-	-	-	-	-
210°	-	6.21	8.44	-	21.68	-
Saybolt Univ. Seconds						
100°	-	176.8	232.1	-	566.0	-
130°	-	-	-	-	-	-
210°	-	46.49	53.87	-	105.3	-
Viscosity Index	-	120.3	137.4	-	144.7	-

Table 126

VINYL ETHER RESIN

Sample No.	598	599	600	601	602	603
Base Oil	Penn 150 Vis Neutral					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	37.67	50.91	-	123.7	-
130°	-	-	-	-	-	-
210°	-	5.96	7.89	-	18.01	-
Saybolt Univ. Seconds						
100°	-	175.2	235.5	-	571.5	-
130°	-	-	-	-	-	-
210°	-	45.69	52.0	-	89.86	-
Viscosity Index	-	111.9	126.2	-	136.6	-

Table 127

PARAFLOW PDX

Sample No.	819	820	821	822	823	824
Base Oil		Mid-Continent 150 Neutral				
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-35°	-40°	-	-25°	-
Cloud Point (°F)	-	+4°	0°	-	+2°	-
Viscosities						
Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 128

SANTOPOUR

Sample No.	849	850	851	852	853	854
Base Oil		Mid-Continent 150 Neutral				
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-35°	-35°	-	-10°	-
Cloud Point (°F)	-	0°	+2°	-	+2°	-
Viscosities						
Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	--	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 129

PARAFLOW 46X

Sample No.	801	802	803	804	805	806
Base Oil		Mid-Continent 150 Neutral				
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-35°	-30°	-	-10°	-
Cloud Point (°F)	-	0°	0°	-	4°	-
Viscosities						
Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 130

ACRYLOID 150

Sample No.	795	796	797	798	799	800
Base Oil			Mid-Continent 150 Neutral			
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-35	-30	-	-20	-
Cloud Point (°F)	-	2	-6	-	-6	-
Viscosities						
Centistokes						
100°	-	38.75	48.25	-	92.74	-
210°	-	5.99	7.53	-	14.79	-
Saybolt Univ. Seconds						
100°	-	180.0	223.3	-	428.4	-
210°	-	45.79	50.80	-	76.93	-
Viscosity Index	-	108.2	124.9	-	140.5	-

Table 131

SANTOPOUR B

Sample No.	873	874	875	876	877	878
Base Oil		Mid Continent 150 Neutral				
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-30	-35	-	-10	-
Cloud Point (°F)	-	-4	0	-	0	-
Viscosities						
Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 132

SANTOPOUR C

Sample No.	807	808	809	810	811	812
Base Oil		Mid-Continent 150 Neutral				
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-25°	-35°	-	-30°	-
Cloud Point (°F)	-	+4°	+4°	-	-2°	-
Viscosities						
Centistokes						
100°	-	36.98	41.96	-	59.58	-
130°	-	-	-	-	-	-
210°	-	5.73	6.60	-	9.67	-
Saybolt Univ. Seconds						
100°	-	172.1	194.5	-	275.5	-
130°	-	-	-	-	-	-
210°	-	44.95	47.75	-	58.08	-
Viscosity Index	-	104.1	118.7	-	137.0	-

Table 133

POUREX

Sample No.	855	856	857	858	859	860
Base Oil	Mid Continent 150 Neutral					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-25°	-35°	-	-25°	-
Cloud Point (°F)	-	+6°	+4°	-		-
Viscosities						
Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 134

SANTOLUBE 203A

Sample No.	879	880	881	882	883	884
Base Oil	Mid Continent 150 Neutral					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-20	-35	-	-35	-
Cloud Point (°F)	-	0	8	-	+12	-
Viscosities						
Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 135

ACRYLOID 722

Sample No.	831	832	833	834	835	836
Base Oil		Mid-Continent 150 Neutral				
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-10°	-20°	-	-30°	-
Cloud Point (°F)	-	+6°	+2°	-	0°	-
Viscosities						
Centistokes						
100°	-	38.45	43.54	-	72.83	-
130°	-	-	-	-	-	-
210°	-	5.98	6.89	-	11.98	-
Saybolt Univ. Seconds						
100°	-	178.7	201.7	-	336.4	-
130°	-	-	-	-	-	-
210°	-	45.76	48.69	-	66.29	-
Viscosity Index	-	109.1	122.6	-	140.8	-

Table 136

30% VINYL ETHER RESIN IN OIL

Sample No.	885	886	887	888	889	890
Base Oil		Mid Continent 150 Neutral				
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	--	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	36.93	40.57	-	55.15	-
130°	-	-	-	-	-	-
210°	-	5.65	6.2	-	8.34	-
Saybolt Univ. Seconds						
100°	-	171.9	188.3	-	254.1	-
130°	-	-	-	-	-	-
210?	-	44.69	46.46	-	53.53	-
Viscosity Index	-	99.95	109.2	-	125.8	-

Table 137

PARATONE

Sample No.	813	814	815	816	817	818
Base Oil			Mid-Continent 150 Neutral			
Per cent Additive	0.5	1.0	3.0	5.10	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	38.54	45.15	-	81.90	-
130°	-	-	-	-	-	-
210°	-	5.88	6.79	-	11.66	-
Saybolt Univ. Seconds						
100°	-	179.2	209.1	-	378.4	-
130°	-	-	-	-	-	-
210°	-	45.44	48.37	-	65.13	-
Viscosity Index	-	104.0	113.9	-	129.6	-

Table 138

ACRYLOID HF 600

Sample No.	837	838	839	840	841	842
Base Oil			Mid-Continent 150 Neutral			
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	39.79	51.83	118.9	-	-
130°	-	-	-	-	-	-
210°	-	6.26	8.46	21.18	-	-
Saybolt Univ. Seconds						
100°	-	184.8	239.8	549.4	-	-
130°	-	-	-	-	-	-
210°	-	46.66	53.94	103.2	-	-
Viscosity Index	-	114.9	134.5	145.1	-	-

Table 139

SANTODEX

Sample No.	843	844	845	846	847	848
Base Oil			Mid-Continent 150 Neutral			
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	38.04	44.88	-	69.96	-
130°	-	-	-	-	-	-
210°	-	5.87	6.97	-	11.00	-
Saybolt Univ. Seconds						
100°	-	176.9	207.8	-	323.2	-
130°	-	-	-	-	-	-
210°	-	45.4	48.94	-	62.74	-
Viscosity Index	-	105.9	120.7	-	136.5	-

Table 140

LOW MOLECULAR WEIGHT POLYBUTENE

Sample No.	861	862	863	864	865	866
Base Oil			Mid-Continent 150 Neutral			
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	38.28	45.49	-	77.79	-
130°	-	-	-	-	-	-
210°	-	5.84	6.84	-	11.12	-
Saybolt Univ. Seconds						
100°	-	177.9	210.7	-	359.4	-
130°	-	-	-	-	-	-
210°	-	45.31	48.53	-	63.17	-
Viscosity Index	-	103.2	114.5	-	128.9	-

Table 141

HIGH MOLECULAR WEIGHT POLYBUTENE

Sample No.	867	868	869	870	871	872
Base Oil			Mid-Continent 150 Neutral			
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	37.89	45.26	-	76.65	-
130°	-	-	-	-	-	-
210°	-	5.83	6.77	-	10.67	-
Saybolt Univ. Seconds						
100°	-	176.2	209.6	-	354.2	-
130°	-	-	-	-	-	-
210°	-	45.28	48.3	-	61.57	-
Viscosity Index	-	104.7	112.9	-	125.6	-

Table 142

ACRYLOID 710

Sample No.	825	826	827	828	829	830
Base Oil		Mid-Continent 150 Neutral				
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	38.17	37.56	-	79.62	-
130°	-	-	-	-	-	-
210°	-	5.96	5.87	-	13.64	-
Saybolt Univ. Seconds						
100°	-	177.5	174.7	-	367.9	-
130°	-	-	-	-	-	-
210°	-	45.69	45.90	-	72.53	-
Viscosity Index	-	109.5	108.2	-	144.2	-

Table 143

SANTOPOUR B

Sample No.	682	683	684	685	686	687
Base Oil	Penn Mineral Seal Oil					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	+15	+10	-	-10	-
Cloud Point (°F)	-	+16	+18	-	+18	-
Viscosities Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 144

PARAFLOW 46X

Sample No.	610	611	612	613	614	615
Base Oil	Penn Mineral Seal Oil					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	+15	+10	-	+10	-
Cloud Point (°F)	-	+18	+16	-	+14	-
Viscosities Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 145

PARAFLOW PDX

Sample No.	628	629	630	631	632	633
Base Oil	Penn. Mineral Seal Oil					
Per cent Additive	-	1.0	3.0	5.0	10.0	-
Pour Point (°F)	-	+15	+10	+5	+5	-
Cloud Point (°F)	-	+18	+18	+16	+16	-
Viscosities Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 146

SANTOLUBE 203 A

Sample No.	694	695	696	697	698	699
Base Oil	Penn Mineral Seal Oil					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	+15	+10	-	+10	-
Cloud Point (°F)	-	+18	+18	-	+20	-
Viscosities Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 147

ACRYLOID 150

Sample No.	604	605	606	607	608	609
Base Oil	Penn Mineral Seal Oil					
Per cent Additive	0.5	1.0	3.0	-	10.0	-
Pour Point (°F)	-	+15	+10	-	+10	-
Cloud Point (°F)	-	+20	+18	-	+16	-
Viscosities Centistokes						
100°	4.53	4.84	6.39	-	14.35	-
130°	-	-	-	-	-	-
210°	1.61	1.71	2.26	-	4.91	-
Saybolt Univ. Seconds						
100°	40.8	41.79	46.75	-	74.73	-
130°	-	-	-	-	--	-
210°	-	-	33.77	-	42.31	-
Viscosity Index	118.9	129.0	175.1	-	225.3	-

Table 148

POUREX

Sample No.	664	665	666	667	668	669
Base Oil	Perm Mineral Seal Oil					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	+15	+15	-	0	-
Cloud Point (°F)	-	20	+18	-	+20	-
Viscosities Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 149

SANTOPOUR

Sample No.	616	617	618	619	620	621
Base Oil	Penn Mineral Seal Oil					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	+15	+15	-	+15	-
Cloud Point (°F)	-	+20	+20	-	+20	-
Viscosities Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 150

SANTOPOUR C

Sample No.	658	659	660	661	662	663
Base Oil	Penn Mineral Seal Oil					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	+20	+10	-	+10	-
Cloud Point (°F)	-	22	+18	-	+16	-
Viscosities Centistokes						
100°	-	4.51	5.32	-	5.58	-
130°	-	-	-	-	-	-
210°	-	1.59	1.81	-	1.95	-
Saybolt Univ. Seconds						
100°	-	40.73	43.32	-	44.16	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	113.4	125.0	-	147.5	-

Table 151

LOW MOLECULAR WEIGHT POLYBUTENE

Sample No.	670	671	672	673	674	675
Base Oil	Penn Mineral Seal Oil					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities Centistokes						
100°	-	4.64	6.03	-	11.03	-
130°						
210°	-	1.63	2.06	-	3.49	-
Saybolt Univ. Seconds						
100°	-	41.15	45.6	-	62.4	-
130°	-	-	-	-	-	-
210°	-	-	33.05	-	37.83	-
Viscosity Index	-	116.5	149.7	-	208.7	-

Table 152

HIGH MOLECULAR WEIGHT POLYBUTENE

Sample No.	676	677	678	679	680	681
Base Oil		Penn Mineral Seal Oil				
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	4.62	5.75	-	10.31	-
130°	-	-	-	-	-	-
210°	-	1.62	1.96	-	3.24	-
Saybolt Univ. Seconds						
100°	-	41.08	44.70	-	59.88	-
130°	-	-	-	-	-	-
210°	-	-	-	-	37.02	-
Viscosity Index	-	115.1	139.8	-	196.2	-

Table 153

VINYL ETHER RESINS

Sample No.	694	695A	696A	697	698A	699
Base Oil	Penn Mineral Seal Oil					
Per cent Additive	-	-	-	-	-	-
Pour Point (°F)	-	1.0	3.0	-	10.0	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	4.34	4.50	-	10.5	-
130°	-	-	-	-	-	-
210°	-	1.53	1.77	-	3.49	-
Saybolt Univ. Seconds						
100°	-	40.19	40.70	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	106.5	170.0	-	220.5	-

Table 154

PARATONE

Sample No.	622	623	624	625	626	627
Base Oil	Penn. Mineral Seal Oil					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	4.67	5.72	-	11.03	-
130°	-	-	-	-	-	-
210°	-	1.60	1.96	-	3.52	-
Saybolt Univ. Seconds						
100°	-	41.24	44.6	-	62.4	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	103.5	155	-	211.7	-

Table 155

ACRYLOID 710

Sample No.	634	635	636	637	638	639
Base Oil	Penn Mineral Seal Oil					
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	4.77	6.01	-	12.7	-
130°	-	-	-	-	-	-
210°	-	1.71	2.17	-	4.57	-
Saybolt Univ. Seconds						
100°	-	41.56	45.53	-	68.49	-
130°	-	-	-	-	-	-
210°	-	-	33.44	-	41.2	-
Viscosity Index	-	133.6	174.8	-	242.3	-

Table 156

ACRYLOID 722

Sample No.	640	641	642	643	644	645
Base Oil		Penn Mineral Seal Oil				
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	4.68	5.48	-	10.54	-
130°	-	-	-	-	-	-
210°	-	1.66	1.95	-	3.7	-
Saybolt Univ. Seconds						
100°	-	41.28	43.84	-	60.69	-
130°	-	-	-	-	-	-
210°	-	-	-	-	38.46	-
Viscosity Index	-	124.0	153.6	-	237.9	-

Table 157

ACRYLOID HF-600

Sample No.	646	647	648	649	650	651
Base Oil		Penn Mineral Seal Oil				
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	4.67	5.99	-	11.18	-
130°	-	-	-	-	-	-
210°	-	1.67	2.19	-	4.14	-
Saybolt Univ. Seconds						
100°	-	41.24	45.47	-	62.95	-
130°	-	-	-	-	-	-
210°	-	-	33.51	-	39.82	-
Viscosity Index	-	127.8	180.0	-	254.8	-

Table 158

SANTODEX

Sample No.	652	653	654	655	656	657
Base Oil		Penn Mineral Seal Oil				
Per cent Additive	-	1.0	3.0	-	10.0	-
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	4.66	6.28	-	10.8	-
130°	-	-	-	-	-	-
210°	-	1.65	2.19	-	3.67	-
Saybolt Univ. Seconds						
100°	-	41.21	46.4	-	61.6	-
130°	-	-	-	-	-	-
210°	-	-	33.51	-	38.37	-
Viscosity Index	-	165.9	190.1	-	230.4	-

Table 159

PARAFLOW 46X

Sample No.	897	898	899	900	901	902
Base Oil	Cadet Z Oil					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Four Point (°F)	-	+15°	-10°	-	-5°	-
Cloud Point (°F)	-	+18°	+18°	-	+14°	-
Viscosities						
Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 160

PARAFLOW PDX

Sample No.	915	916	917	918	919	920
Base Oil		Cadet Z Oil				
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	+15°	-5°	-	-5°	-
Cloud Point (°F)	-	+20°	+16°	-	+16°	-
Viscosities						
Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 161

ACRYLOID 150

Sample No.	891	892	893	894	895	896
Base Oil	Cadet Z Oil					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	+5°	0°	-	+5°	-
Gloud Point (°F)	-	+26	24°	-	+16°	-
Viscosities						
Centistokes						
100°	-	8.21	11.24	-	25.08	-
130°	-	-	-	-	-	-
210°	-	2.33	3.17	-	6.84	-
Saybolt Univ. Seconds						
100°	-	52.71	63.16	-	119.2	-
130°	-	-	-	-	-	-
210°	-	34.03	36.79	-	48.53	-
Viscosity Index	-	109.2	165.2	-	182.3	-

Table 162

SANTOPOUR C

Sample No.	903	904	905	906	907	908
Base Oil		Cadet Z Oil				
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	+10°	+5°	-	+5°	-
Cloud Point (°F)	-	+18°	+20°	-	+14°	-
Viscosities						
Centistokes						
100°	-	27.22	9.26	-	14.92	-
130°	-	-	-	-	-	-
210°	-	2.19	2.63	-	4.17	-
Saybolt Univ. Seconds						
100°	-	51.08	56.28	-	76.9	-
130°	-	-	-	-	-	-
210°	-	33.51	35.06	-	39.91	-
Viscosity Index	-	95.61	133.1	-	202.2	-

Table 163

SANTOPOUR

Sample No.	945	946	947	948	949	950
Base Oil	Cadet Z Oil					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	+15	+5	-	+5	-
Cloud Point (°F)	-	+18	+24	-	+20	-
Viscosities						
Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 164

SANTOLUBE 203A

Sample No.	975	976	977	978	979	980
Base Oil	Cadet Z Oil					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	+10	+10	-	+10	-
Cloud Point (°F)	-	+22	+18	-	+28	-
Viscosities						
Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 165

SANTOPOUR B

Sample No.	969	970	971	972	973	974
Base Oil	Cadet Z Oil					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	+15	+15	-	-40	-
Cloud Point (°F)	-	+24	+18	-	+2	-
Viscosities						
Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 166

POUREX

Sample No.	951	952	953	954	955	956
Base Oil	Cadet Z Oil					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	+15	+15	-	-15	-
Cloud Point (°F)	-	+20	+18	-	+20	-
Viscosities						
Centistokes						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Saybolt Univ. Seconds						
100°	-	-	-	-	-	-
130°	-	-	-	-	-	-
210°	-	-	-	-	-	-
Viscosity Index	-	-	-	-	-	-

Table 167

PARATONE

Sample No.	909	910	911	912	913	914
Base Oil		Cadet Z Oil				
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	8.26	9.92	-	19.45	-
130°	-	-	-	-	-	-
210°	-	2.32	2.74	-	4.97	-
Saybolt Univ. Seconds						
100°	-	52.88	58.53	-	95.19	-
130°	-	-	-	-	-	-
210°	-	33.99	35.41	-	42.5	-
Viscosity Index	-	103.5	132.4	-	184.0	-

Table 168

ACRYLOID 710

Sample No.	921	922	923	924	925	926
Base Oil		Cadet Z Oil				
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	8.41	10.79	-	23.46	-
130°	-	-	-	-	-	-
210°	-	2.40	3.11	-	6.66	-
Saybolt Univ. Seconds						
100°	-	53.39	61.57	-	112.3	-
130°	-	-	-	-	-	-
210°	-	34.28	36.6	-	47.94	-
Viscosity Index	-	116.9	168.0	-	186.5	-

Table 169

ACRYLOID 722

Sample No.	927	928	929	930	931	932
Base Oil	Cadet Z Oil					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	7.96	9.65	-	18.39	-
130°	-	-	-	-	-	-
210°	-	2.27	2.75	-	5.13	-
Saybolt Univ. Seconds						
100°	-	51.87	57.61	-	90.8	-
130°	-	-	-	-	-	-
210°	-	33.81	35.44	-	43.02	-
Viscosity Index	-	105.0	143.1	-	195.2	-

Table 170

ACRYLOID HF 600

Sample No.	933	934	935	936	937	938
Base Oil	Cadet Z Oil					
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	9.05	13.49	-	38.18	-
130°	-	-	-	-	-	-
210°	-	2.61	3.94	-	11.08	-
Saybolt Univ. Seconds						
100°	-	55.57	71.46	-	177.5	-
130°	-	-	-	-	-	-
210°	-	34.99	39.19	-	63.03	-
Viscosity Index	-	136.8	172.2	-	207.4	-

Table 171

SANTODEX

Sample No.	939	940	941	942	943	944
Base Oil		Cadet 2 Oil				
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	7.93	10.17	-	18.08	-
130°	-	-	-	-	-	-
210°	-	2.26	2.87	-	4.93	-
Saybolt Univ. Seconds						
100°	-	51.77	59.39	-	89.53	-
130°	-	-	-	-	-	-
210°	-	33.77	35.83	-	42.38	-
Viscosity Index	-	104.1	147.8	-	194.1	-

Table 172

LOW MOLECULAR WEIGHT POLYBUTENE

Sample No.	957	958	959	960	961	962
Base Oil		Cadet Z Oil				
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	8.17	9.83	-	20.13	-
130°	-	-	-	-	-	-
210°	-	2.29	2.71	-	5.13	-
Saybolt Univ. Seconds						
100°	-	52.58	58.22	-	98.03	-
130°	-	-	-	-	-	-
210°	-	33.88	35.31	-	43.02	-
Viscosity Index	-	100.9	129.7	-	182.5	-

Table 173

HIGH MOLECULAR WEIGHT POLYBUTENE

Sample No.	963	964	965	966	967	968
Base Oil		Cadet Z Oil				
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	7.94	9.68	-	18.39	-
130°	-	-	-	-	-	-
210°	-	2.24	2.67	-	4.61	-
Saybolt Univ. Seconds						
100°	-	51.8	57.71	-	90.80	-
130°	-	-	-	-	-	-
210°	-	33.7	35.18	-	41.33	-
Viscosity Index	-	98.13	126.8	-	181.9	-

Table 174

30% VINYL ETHER RESIN

Sample No.	981	982	983	984	985	986
Base Oil		Cadet Z Oil				
Per cent Additive	0.5	1.0	3.0	5.0	10.0	15.0
Pour Point (°F)	-	-	-	-	-	-
Cloud Point (°F)	-	-	-	-	-	-
Viscosities						
Centistokes						
100°	-	7.69	8.73	-	13.61	-
130°	-	-	-	-	-	-
210°	-	2.18	2.44	-	3.59	-
Saybolt Univ. Seconds						
100°	-	50.98	54.48	-	71.92	-
130°	-	-	-	-	-	-
210°	-	33.48	34.42	-	38.13	-
Viscosity Index	-	94.58	113.2	-	168.3	-

B. Experimental Procedure

1. Extraction of Commercial Additives from Oil Blends

The following procedure for the extraction of Acryloid 150 from the oil blend, in which form it is marketed, is an example of the method used for the isolation of commercial additives. Eighty to ninety grams of the material were dissolved in diethyl ether at room temperature with stirring. When the additive had completely dissolved, 40 milliliters of absolute ethanol were added slowly to precipitate the polymeric material. The upper solvent layer bearing the oil fraction was decanted and centrifuged to assure complete separation. The polymer was redissolved in ether and the extraction procedure repeated. After ten reprecipitations, no oil appeared in the solvent layer. The solvent was then stripped from the polymer extract and the combined oil-bearing solvent layers yielded the oil and additive fractions.

2. Cryoscopic Determination of Molecular Weight

The weighed subject polymer was dissolved in a three-five per cent concentration in sym-difluorotetrachloroethane by refluxing. After determination of the weight of solvent used, an aliquot of the solution was placed into a small unsilvered dewar flask having a side arm for evacuation of the jacket. A calibrated Beckmann thermometer and a vertical stainless steel helical stirrer were completely immersed in the solution. The stirring coil was adjusted in place around the Beckmann thermometer bulb so that it did not touch any surface during its stroke. Mechanical stirring was accomplished with a standard windshield wiper motor driven by a Cenco oil pump and adapted for a vertical reciprocating stroke. The

speed of stirring was adjusted to 60 strokes per minute by means of a needle valve in the pump line. The dewar flask was immersed in an unsilvered dewar flask containing water at a temperature approximately 4° C below the expected freezing point. The jacket of the flask containing the cryoscopic solution was evacuated with an oil pump and the cooling rate adjusted to about 0.15 degrees per minute by control of the jacket pressure with a needle valve. Readings were taken at one minute intervals initially and at 15 second intervals in the vicinity of the expected freezing point.

The molecular weight of the solute was calculated using the following equation:

$$\overline{MW} = \frac{1000 W_1 K}{(T_b - T_a) W_2}$$

$\overline{MW}$ = average molecular weight of solute

K = predetermined molal freezing point constant; °C/(mole of solute) (1000 gm solvent)

W_1 = weight of solute; gm

W_2 = weight of solvent; gm

T_a = freezing point of solvent; °C

T_b = freezing point of solution, °C

3. Exhaustive Fractionation of Dodecyl Polymethacrylate

A sample of crude dodecyl polymethacrylate to be fractionated was obtained by polymerization for 78 hours of 2 moles (508 gm) of dodecyl

methacrylate in 4 moles (616 gm) of carbon tetrachloride containing 5.08 gm of benzoyl peroxide at 70° C. After stripping of the solvent under vacuum at 105° C, the polymeric residue was dissolved in 2,000 ml of benzene (0.25 gm/ml) in the following way: after treatment with 500 ml of cold benzene to saturation the remaining polymer was dissolved in 250 ml of benzene with refluxing. The flask was then washed with five separate 250 ml portions of benzene, all solutions being combined in a three liter separatory funnel. The final concentration of polymer was approximately 0.25 gm/ml of benzene.

One liter of methanol was added to the benzene solution; the mixture was thoroughly shaken and allowed to stand for three hours at which time layer separation was complete. The lower layer was separated as fraction No. 12, Figure 5.

One liter of methanol was added to the upper layer, fraction No. 21, and after shaking, the mixture was allowed to stand overnight. During this period a lower layer of approximately 5 ml separated. This lower layer, fraction No. 22, was added to fraction No. 12. The upper layer was fraction No. 31 in the separation scheme.

The solvents were removed from fractions Nos. 12 and 31 by stripping at a maximum oil bath temperature of 105° C and at pressures ranging from atmospheric to approximately 15 mm. The yields were: fraction No. 12 = 468.3 gm, fraction No. 31 = 56.2 gm. Fraction No. 12 is the polymer which has been referred to as the "unfractionated" material with an average molecular weight of 4,000, since it represents the original polymerization product from which only monomer and other very low molecular weight material has been removed.

Fraction No. 12 was dissolved in 1870 ml of benzene, 0.25 gm/ml, and placed in a separatory funnel. Complete transfer of the polymer was insured by dissolving the major portion in 500 ml of the solvent, refluxing with an additional 500 ml and finally washing the flask with portions of the remaining 870 ml of benzene. All subsequent transfers were made subject to these precautions.

Methanol was added with shaking in 50 ml increments until schlieren became pronounced and then in 25 ml increments until turbidity persisted. A total of 600 ml of methanol was used. The mixture was allowed to stand until phase separation was complete. The lower layer, fraction No. 13, was separated from the upper layer, fraction No. 22, after which the solvents were removed as previously described. Yields: fraction No. 13 = 417.4 gm, fraction No. 22 = 58.6 gm.

The remaining fractionations were made essentially as described for fraction No. 12, each product being treated according to the scheme presented in Figure 5. Where the combination of fractions is indicated, e.g., fraction No. 23, this was carried out prior to the removal of solvent. Slight modifications were necessary. Smaller samples e.g., fraction No. 22, were dissolved in benzene in concentrations of 0.1 gm/ml. In compensation, methanol was added in proportionately smaller increments. In the advanced stages of the separation where most of the low molecular weight material had been already eliminated, it was necessary to use methanol-acetone mixtures as the precipitant since the polymers were too insoluble in methanol alone to give adequate fractionation.

The final fractions were freed of solvent in a vacuum desiccator as follows: The open top of the desiccator was fitted with a two-holed

rubber stopper containing a capillary tube and an outlet tube to a vacuum pump. A layer of oil was placed in the bottom of the desiccator to promote heat transfer and the desiccator was placed in an oil bath on a hot plate fitted with a variable transformer. The samples to be treated were placed in cream jars, submerged in the oil in the desiccator so that the capillary dipped well below the surface of the liquid. The solvent was removed at pressures of from 100 to 2 mm at oil temperatures inside the desiccator of 85-100° C.

4. Dewaxing of Pennsylvania 150 Neutral Oil

A solution composed of 750 ml of Pennsylvania 150 Neutral oil, pour point 5° F, 2100 ml of toluene and 900 ml of acetone (oil:solvent = 1:4 by volume; solvent = toluene:acetone = 7:3 by volume) were placed into a three necked three liter round bottomed flask fitted with a stirrer, filter stick and thermometer well. The flask was immersed in a cooling bath containing alcohol and water in a ratio yielding a freezing point of -65° F. The stirrer was started and sufficient dry ice added to the bath to form a slurry. The oil mixture was stirred for one hour after its temperature had reached -60° F. The stirrer was stopped and 250 gm of filter cell added to the mixture, which was then stirred until the filter cell had completely dispersed. The stirrer was replaced with a gas inlet tube fitted to a dry nitrogen tank having a reduction valve and the mixture was allowed to stand for one-half hour. All rubber stoppers were firmly wired to the flask and a nitrogen pressure of five pounds introduced. The dewaxed oil solution, which then rose through the filter stick, was collected in a filter flask. It was occasionally necessary to increase the pressure

to twelve pounds to maintain an appreciable flow rate. Stripping of the solvent from the oil solution yielded a Pennsylvania 150 Neutral oil with a cloud and pour point lower than -50° F.

5. Determination of Micro Pour Points

Micro pour point determinations were carried out in an alcohol cooling bath composed of a glass tank fitted into a wooden insulating box having Lucite windows to facilitate the constant observation of immersed samples. The one inch space between tank and box was packed with rock wool. Approximately one gram oil samples were placed in one-half dram screw-capped vials fitted with Neoprene rubber gaskets and were preheated in a water bath to 212° F. The vials, after cooling to room temperature, were put into holders designed to permit tilting of the samples when submerged in the bath. A cooling rate of two degrees per two minutes, or one degree per minute, was accomplished by the addition of sufficient dry ice to cool the alcohol bath two degrees Fahrenheit and the holding of the bath at that temperature for two minutes. The alcohol was stirred at all times. Cloud points were taken as the temperature to which the bath had been cooled when the s ample became cloudy, while the pour point was the temperature to which the bath had been cooled when the sample would not flow when tilted to the horizontal for five seconds.

Samples having cloud and pour points above room temperature were tested in a shallow porcelain pan water bath. The bath containing the samples was heated to its boiling point and allowed to cool with stirring to approximately 20° F above the highest expected cloud point. A cooling rate of two degrees Fahrenheit per two minutes was then initiated with shaved

ice.

6. Preparation of Wax Crystal Slides

The normal paraffins were crystallized from their oil solutions on the sample slides. The samples to be observed were preheated to 212° F and placed on the slide while hot. Well defined crystals could be obtained only when a thick oil sample was used. After the covering of the oil drop with a cover glass, samples with cloud points above room temperature were placed on a hot bar at a temperature greater than 20° F above that crystallization temperature. Cooling was accomplished by moving the slide down the hot bar one slide width every five minutes at first and progressively longer periods of time as the expected cloud point was approached. When initial crystallization was observed, the samples were not moved for at least twenty minutes and were left at lower temperatures for a minimum of fifteen minutes.

Samples with cloud points below room temperature were allowed to cool to room temperature on the slide and were then cooled (to their respective cloud points) on the microscope cold stage to be described.

7. Microscope Cold Stage

The cold stage used for the cooling and observation of wax-oil samples with cloud points below room temperature was composed of an aluminum block to which was attached a partially hollowed aluminum rod. The sample slide was placed on top of the block through which a small hole had been drilled to facilitate light passage through the sample. Both the block and the rod were coated with thick layers of asbestos for insulation. The stage was cooled by the passage of precooled dry nitrogen into the rod. A small

gas outlet hole at a point above the oil sample prevented frosting of the slide by providing a dry atmosphere. Nitrogen was precooled by passage through coils immersed in a Dewar flask containing a dry ice-trichloroethylene bath. A solenoid valve in the gas line between the tank and the cooling bath provided a temperature control when used in conjunction with the relay system of a Leeds and Northrup Micromax and a thermocouple imbedded in the aluminum block. The thermocouple and the Micromax also recorded the cold stage temperature.

A cooling rate of two degrees Fahrenheit per two minutes was attained by moving the Micromax black indicator arrow each two minutes a number of millivolts on the scale equivalent to two degrees Fahrenheit. When the red arrow, the stage temperature indicator, was at a higher reading than the black arrow, the relay system activated the solenoid valve permitting the passage of the cooling gas. When the red arrow indicated that the stage had reached the desired temperature; i.e., the two arrows read the same temperature, the solenoid valve closed. Control was maintained within $\pm$ 1° F.

8. Preparation of Condensation Polymers

The preparation of poly-1,2-tetradecylene succinate will be described as an example of the procedure used in the synthesis of condensation polymers. Reactions were carried in a 100 ml, three necked, round bottomed flask one neck of which was replaced by an eight inch air condensing tube terminating in a one necked receiver. When 11.5 g (0.05 moles) of 1,2-tetradecandiol, prepared according to the procedure of Swern, Billen

and Scanlan[20], and 5.00 gm (0.05 moles) of succinic anhydride were heated at atmospheric pressure with an oil bath at 170° C and stirred for 48 hours, approximately 1.5 gm of water distilled from the reaction and a liquid amber-colored product resulted. The synthesis was then continued at 100 mm pressure and 170° C with nitrogen ebullition and stirring for 24 hours. At the end of this time the pressure was reduced to approximately one millimeter and the reaction continued for five days. The product was then a very viscous dark brown liquid. The lower molecular weight fractions of the yield were removed by solution of the polymer in 25 ml of carbon tetrachloride and precipitation of the higher molecular weight fractions with methyl alcohol. The latter material was returned to the flask and heated at 170° C and one millimeter pressure with nitrogen ebullition and stirring until the product had become a soft rubbery solid difficultlysoluble in carbon tetrachloride. For different preparations this time varied from 12 to 48 hours.

Variations in procedure were used in the several polymerizations. In those instances where phthalic polyesters were prepared, an initial reaction temperature of 150° C was necessary to minimize the loss of anhydride by sublimation. Since the reaction conditions were designed to provide optimum conditions for the removal of water without distillation of reactants or products, a considerable range of variations in time and temperatures could be applied.

C. Habits of Pure n-Paraffin Wax Crystallized from Dewaxed Pennsylvania 150 Neutral Oil in the Presence and Absence of Depressants

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Figure 36

6.00% n-Eicosane

Cloud Point 36° F Pour Point 30° F

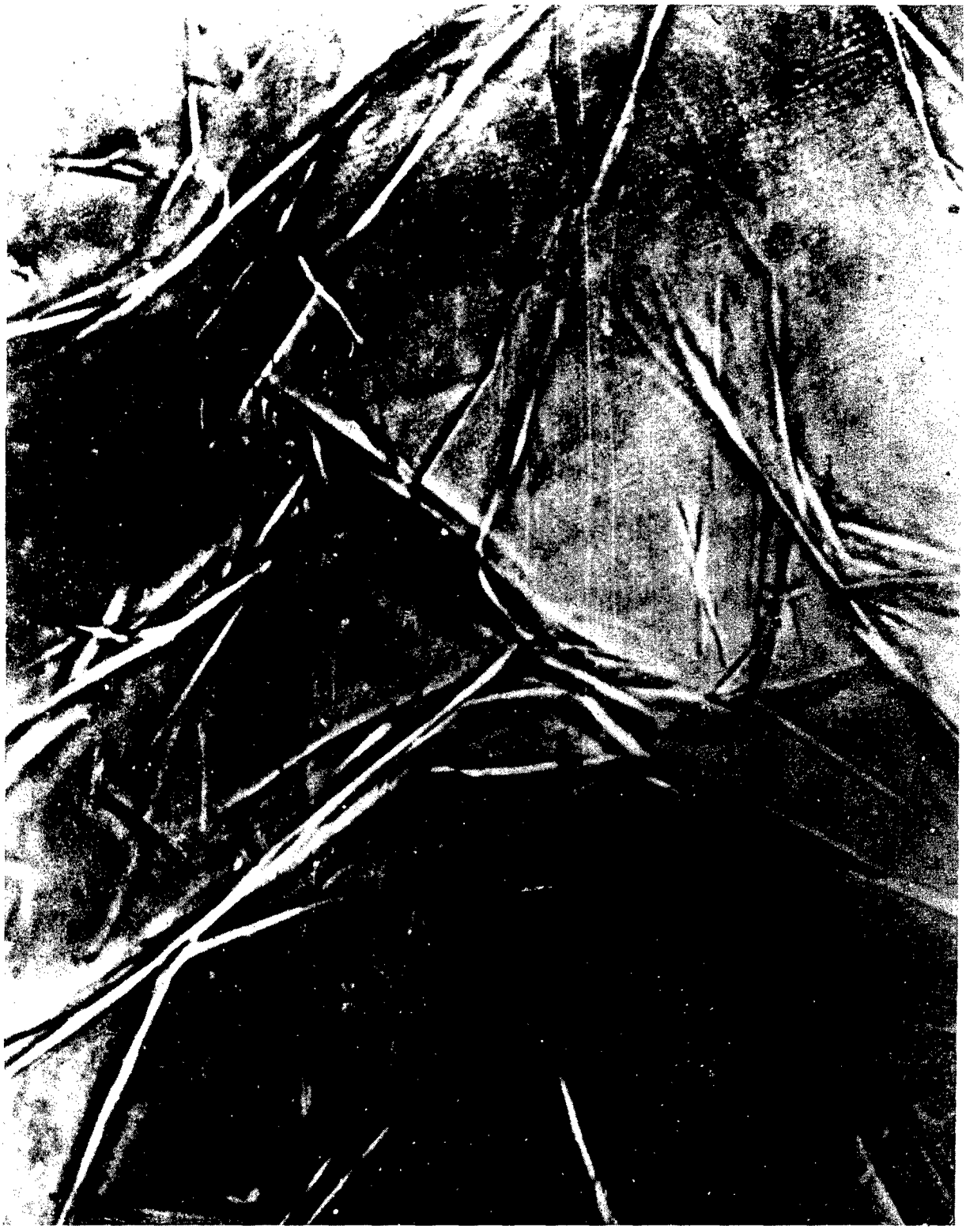


Figure 37

8.60% n-Heneicosane

Cloud Point 58° F Pour Point 54° F



Figure 38

8.00% n-Docosane

Cloud Point 58° F Pour Point 54° F



Figure 39

7.60 % n-Tricosane

Cloud Point 62° F Pour Point 60° F

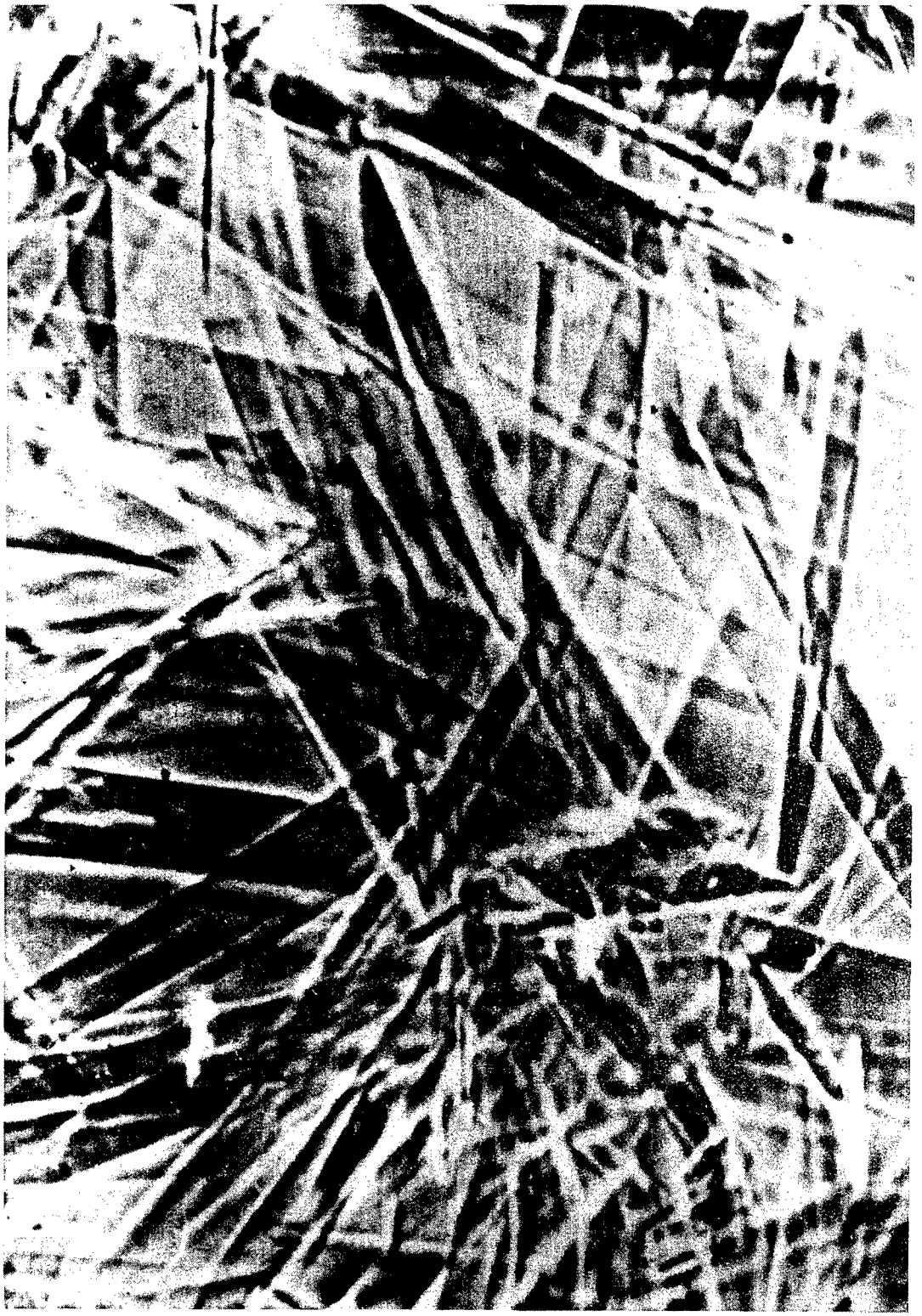


Figure 40

8.00% n-Tetracosane

Cloud Point 72° F Pour Point 70° F



Figure 41

8.00% n-Pentacosane

Cloud Point 76° F Pour Point 72° F

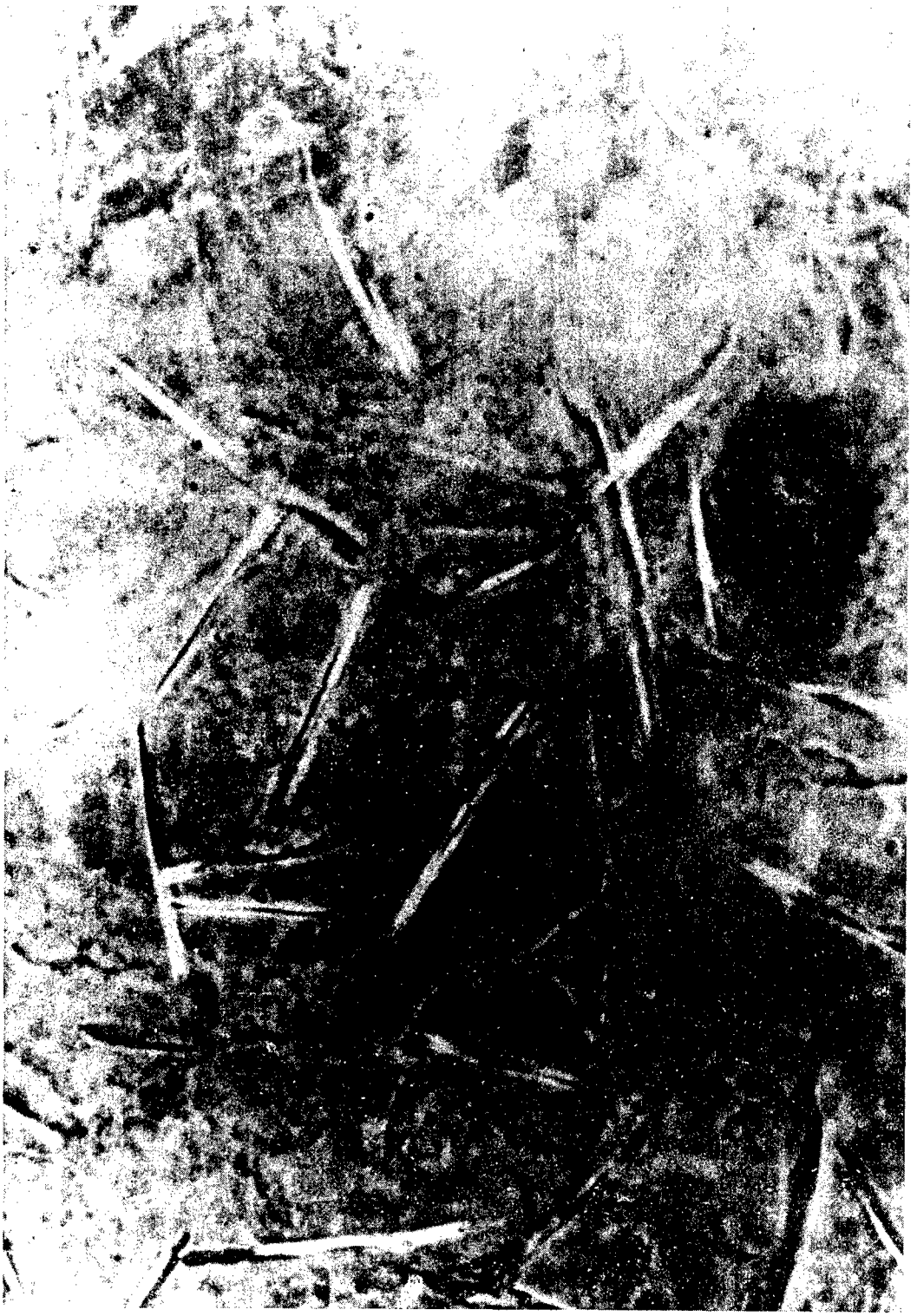


Figure 42

8.00% n-Heptacosane

Cloud Point 88° F Pour Point 86° F



Figure 43

5.00% n-Octacosane

Cloud Point 82° F Pour Point 80° F



Figure 44

7.70% n-Octacosane

Cloud Point 92° F Pour Point 88° F



Figure 45

8.00% n-Triacontane

Cloud Point 106° F Pour Point 102° F



Figure 46

5.00% n-Eicosane

3.50% Hexadecyl Polymethacrylate

Cloud Point 28° F Pour Point Depression Exhibited



Figure 47

8.00% n-Heneicosane

3.50% Hexadecyl Polymethacrylate

Cloud Point 52° F Pour Point Depression Exhibited



Figure 48

8.00% n-Docosane

3.50% Hexadecyl Polymethacrylate

Cloud Point 58° F Pour Point Depression Exhibited



Figure 49

8.00% n-Tricosane

3.50% Hexadecyl Polymethacrylate

Cloud Point 62° F Pour Point Depression Exhibited



Figure 50

8.00% n-Tetracosane

3.50% Hexadecyl Polymethacrylate

Cloud Point 72° F Pour Point Depression Exhibited



Figure 51

8.00% n-Pentacosane

3.50% Hexadecyl Polymethacrylate

Cloud Point 76° F Pour Point Depression Exhibited



Figure 52

8.00% n-Heptacosane

3.50% Hexadecyl Polymethacrylate

Cloud Point 88° F Pour Point not determined



Figure 53

8.00% n-Triacontane

3.50% Hexadecyl Polymethacrylate

Cloud Point 106° F Pour Point not determined



Figure 54

8.00% n-Octacosane

3.50% Decyl Polymethacrylate

Cloud Point 88° F Pour Point 84° F



Figure 55

8.00% n-Octacosane

8.10% Undecyl Polymethacrylate

Cloud Point-94°F Pour Point-90° F



Figure 56

5.00% n-Octacosane

3.50% Octyl Polyacrylate

Cloud Point 84° F Pour Point 80° F



Figure 57

8.00% n-Octacosane

3.50% Octyl Polyacrylate

Cloud Point 92° F Pour Point 90° F



Figure 58

8.00% n-Octacosane

3.50% Decyl Polyacrylate

Cloud Point 92° F Pour Point 90° F



Figure 59

8.00% n-Octacosane

3.50% Viscosity Index Improver A

Cloud Point 92° F Pour Point 90° F



Figure oO

8.00% n-Octacosane

3.50% Low M.W. Polybutene

Cloud Point 88° F Pour Point 84° F



Figure 61

5.00% n-Eicosane

3.50% Dodecyl Polymethacrylate

Cloud Point 28° F Pour Point Depression Exhibited

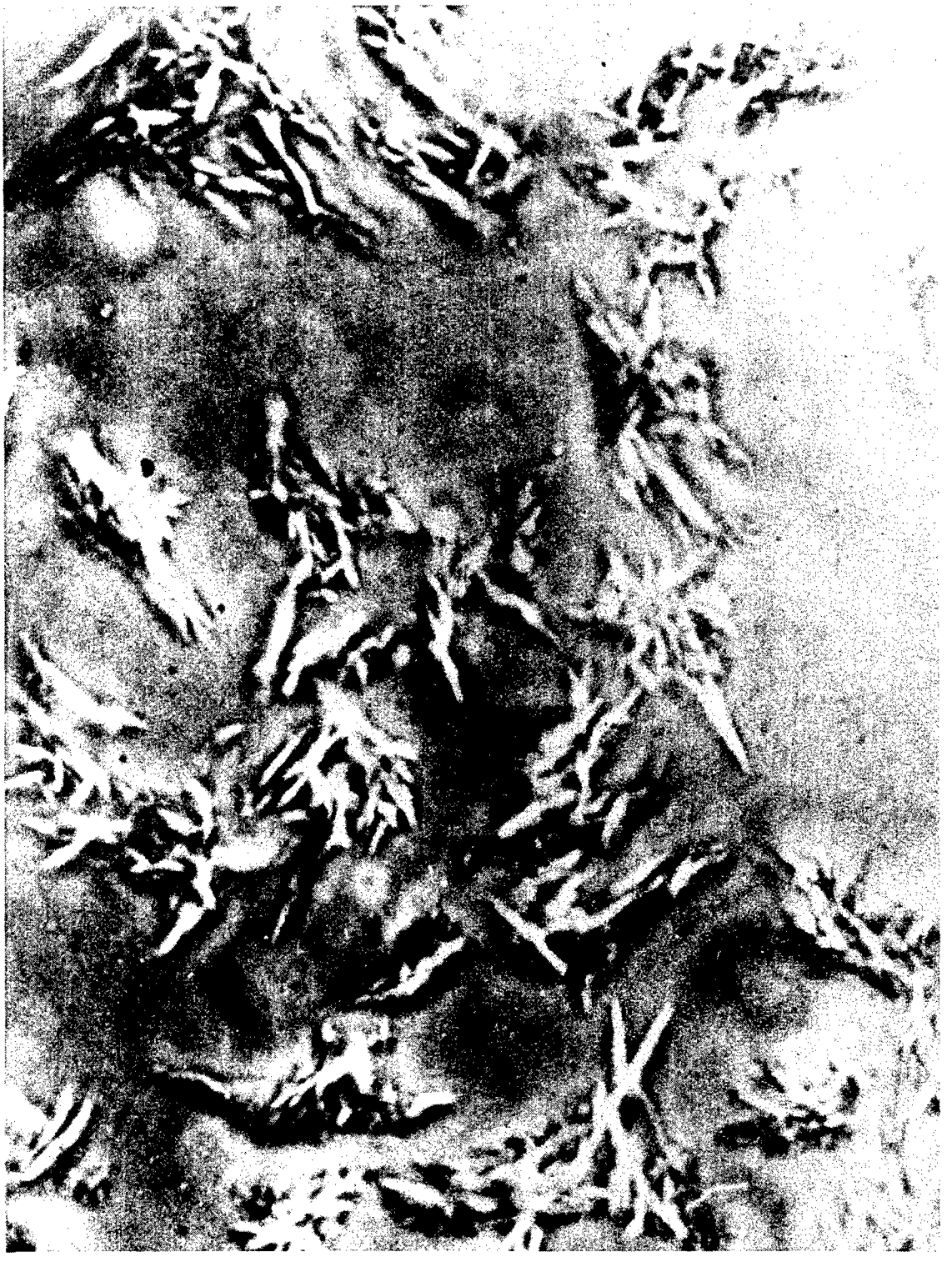


Figure 62

5.00% n-Eicosane

3.50% Tetradecyl Polymethacrylate

Cloud Point 24° F Pour Point Depression Exhibited



Figure 63

15.00% n-Eicosane

6.40% Tetradecyl Polymethacrylate

Cloud Point 62° F Pour Point Depression Exhibited



Figure 64

3.25% n-Octacosane

3.50% Dodecyl Polymethacrylate

Cloud Point 72° F Pour Point Depression Exhibited



Figure 65

8.70% n-Octacosane

3.50% Dodecyl Polymethacrylate

Cloud Point 92° F Pour Point 90° F

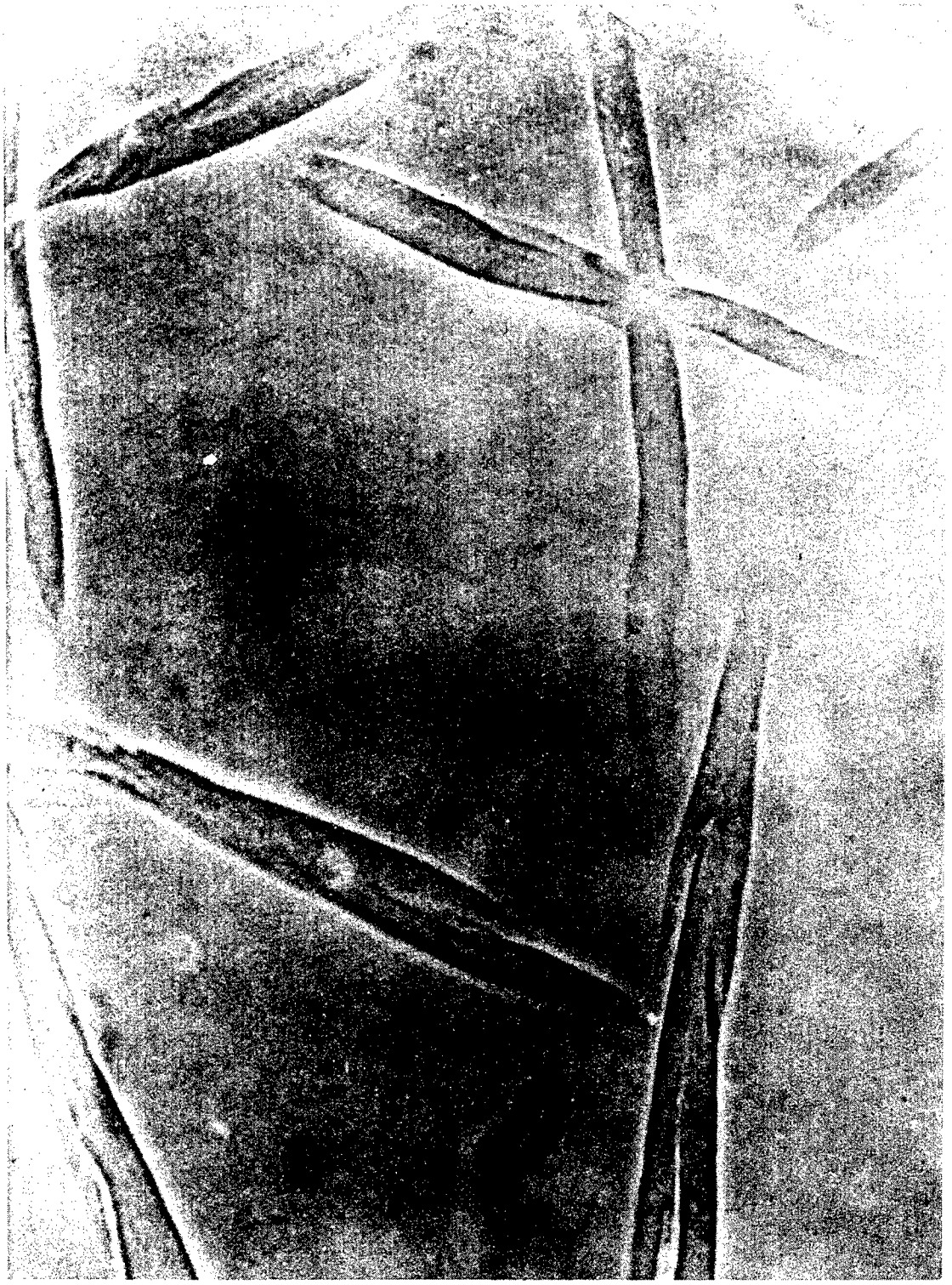


Figure 66

3.00% n-Octacosane

3.50% Tetradecyl Polymethacrylate

Cloud Point 72° F Pour Point Depression Exhibited



Figure 67

5.00% n-Octacosane

3.50% Tetradecyl Polymethacrylate

Cloud Point 82° F Pour Point Depression Exhibited

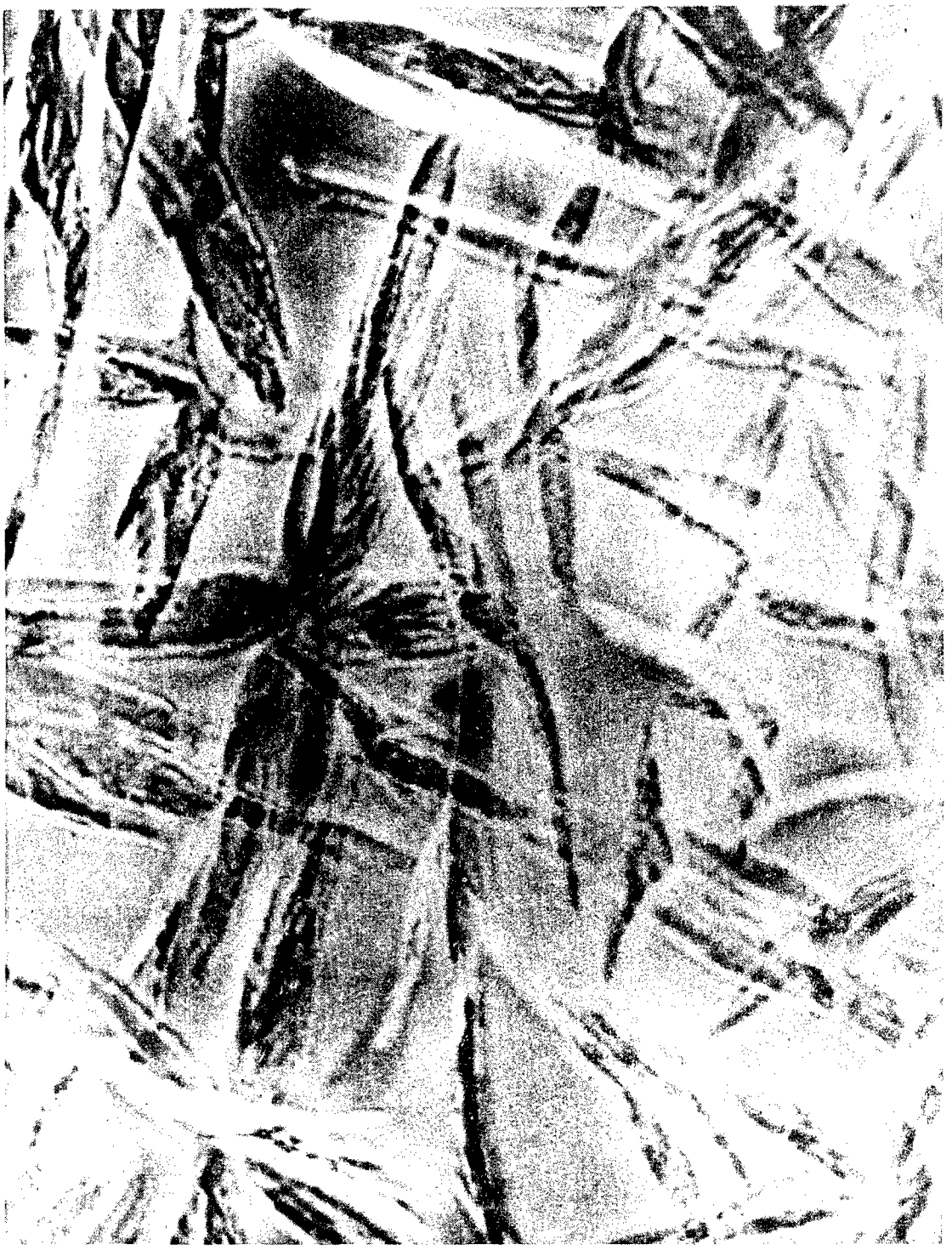


Figure 68

6.50% n-Octacosane

3.50% Tetradecyl Polymethacrylate

Cloud Point 88° F Pour Point 84° F

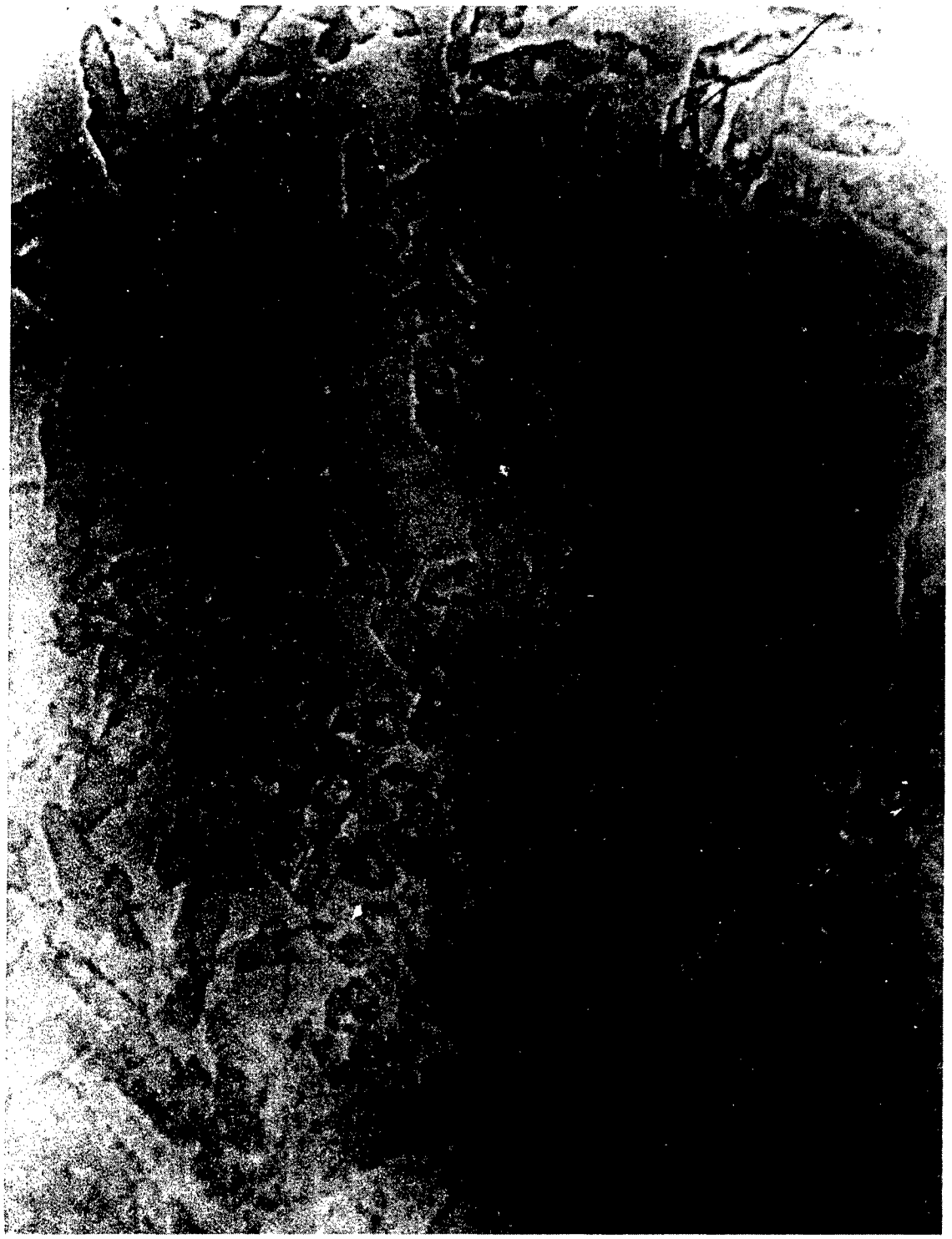


Figure 69

8.00% n-Octacosane

3.50% Tetradecyl Polymethacrylate

Cloud Point 92° F Pour Point 88° F

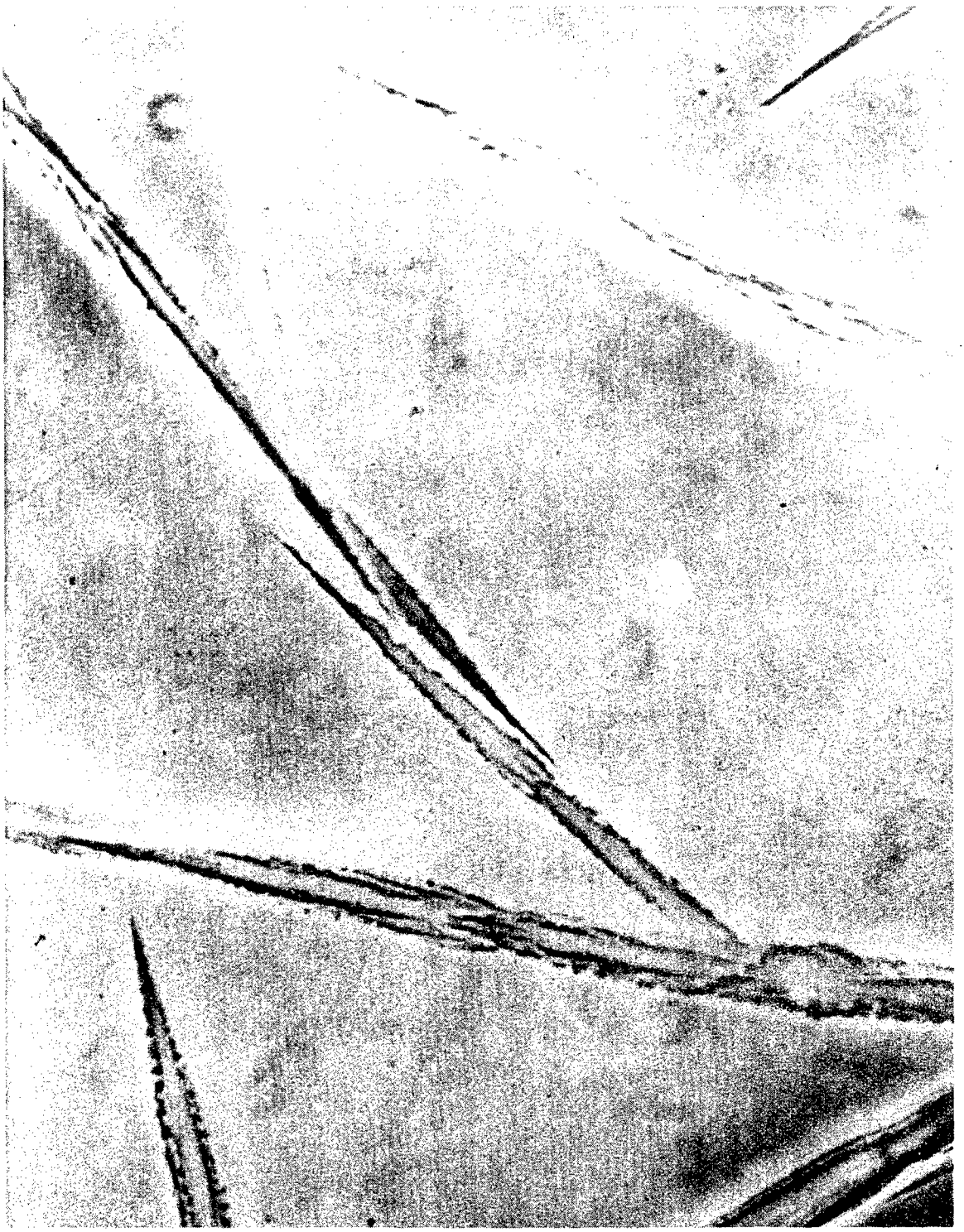


Figure 70

5.50% n-Octacosane

3.50% Hexadecyl Polymethacrylate

Cloud Point 84° F Pour Point Depression Exhibited

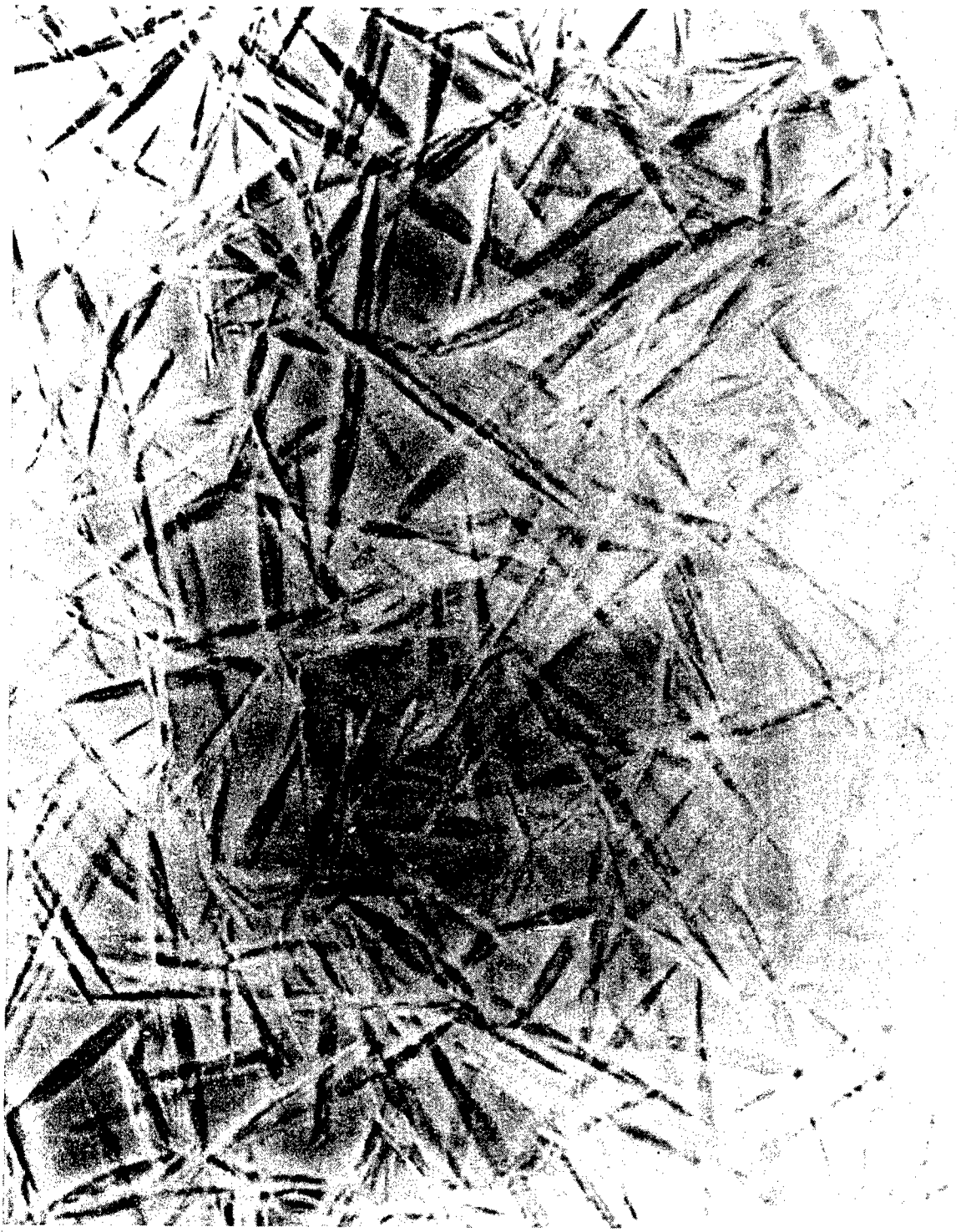


Figure 71

8.00% n-Octacosane

3.50% Hexadecyl Polymethacrylate

Cloud Point 92° F Pour Point 86° F



Figure 72

8.00% n-Octacosane

3.50% Commercial Depressant A

Cloud Point 90° F Pour Point Depression Exhibited



Figure 73

8.00% n-Octacosane

3.50% Commercial Depressant B

Cloud Point 88° F Pour Point Depression Exhibited

D. Manuscript of Paper Presented Before the Society of Rheology, Chicago, October 27, 1951

THE RHEOLOGY OF A LUBRICATING OIL AT TEMPERATURES BELOW THE POUR POINT[15]

1. INTRODUCTION

Many petroleum-base lubricating oils become rigid solids or semi-solids at temperatures below their cloud points. A widely used test for evaluating the low temperature usefulness of an oil, devised by the American Society for Testing Materials, defines the pour point as that temperature below which the oil will not pour from a standard vessel under rigidly specified conditions of cooling and manipulation[21]. Previous investigations of the rheology of petroleum oils in the temperature region below the pour point have been reviewed by Bondi[22], who comments that the field of low temperature viscometry of lubricating oils is in an exploratory stage in which each investigator has devised a flow measuring apparatus for his own particular aims. For the most part the instruments used have been viscometers of a capillary type. This paper presents observations on the behavior of a lubricating oil below the pour point in a rotational, concentric-cylinder viscometer, and some aspects of the rheology of a suspension of a normal paraffin hydrocarbon in a petroleum oil.

2. EXPERIMENTAL METHODS

The low temperature studies in this investigation have been made with a rotational viscometer patterned after that described by Green[23]. The oil is situated in an annular space between coaxial cylinders, the outer of which (the cup) rotates at a number of constant velocities in 40 equal increments to 400 rpm. The inner cylinder (the bob) is attached to a torsion spring which permits measurement of the torque imparted to it. The measurements have been reduced to absolute units by means of the following relations derivable from the hydrodynamics of Newtonian flow under these conditions:

The shearing stress, S, and rate of shear, $\dot{e}$, are given by,

$$(1) \qquad S = \frac{T}{2\pi r^2 h_e}$$

and

$$(2) \qquad \dot{e} = \frac{2R_c^2 R_b^2}{R_c^2 - R_b^2} \cdot \frac{(\omega)}{r^2}$$

where the symbols appearing are defined as follows:

T = torque on the bob

h_e = effective height of the bob and contains an end correction

R_c = radius of the cup

R_b = radius of the bob

$r = \frac{R_c + R_b}{2}$ = average radial distance of the sheared sample from the axis of rotation

(ω) = angular velocity of the cup

In order that the shear rate attainable might be extended, two cups having radii of 1.40 cm and 1.50 cm, giving cup to bob clearances of 1.0 mm and 2.0 mm, respectively, have been employed. In the data presented the cup used is indicated by the use of solid symbols for the former and open symbols for the latter.

The low temperature measurements were made at -25° C and -30° C, such temperatures being maintained by means of a special bath surrounding the viscometer cup and an external cooling system. The viscometer cup was situated in a steel bath 5.5 inches in diameter and 9.5 inches high, insulated with two inches of glass wool. Through the bath was circulated a coolant, isopropyl alcohol, continuously pumped through coils in a cryostat containing an alcohol water mixture freezing about 10° C below the temperature of the experiment and cooled with dry ice. Variations in temperatures were opposed by a 125 watt electric heater in the pumping system transferring heat to the bath liquid. The heater was operated intermittently by the control circuits of a Micromax recording potentiometer which recorded the output of a 3-junction thermopile in the viscometer bath. Under steady state conditions temperature control of $\pm$ 0.25° C was obtained; however, in the initial stages of shearing at high rates there was observed a slight rise in temperature, the degree of control being estimated at $\pm$ 0.5° C. A plastic frost shield extending from the bath cover to the bob bearing sleeve was flooded with precooled dry nitrogen, preventing moisture condensation on the sample and excessive heat loss through the bob shaft.

Since the thermal history of an oil is known to affect its low temperature rheology[24], the rate of cooling the sample to the temperature of the experiment was controlled by the rate of addition of dry ice to the cryostat, and unless otherwise noted the samples were cooled at a rate of 1° C per minute and maintained at the temperature of the experiment for 30 minutes before shearing.

This investigation was made on one oil designated Pennsylvania 150 Neutral, dewaxed to a pour point of -15° C. All samples were obtained from a single 50 gallon lot, being withdrawn in quantities of about 1 liter and heated to 100° C before use.

A high pour point oil was prepared by the addition of Eastman white label grade n-octacosane to the above oil. This system was studied with a Stormer viscometer with cylindrical cup and bob modified according to Fischer[16]. The sample was heated to solution of the wax at 60° C, placed in the viscometer cup and, with the bob in place, cooled to 30° C, at which temperature it was quite solid.

3. RESULTS AND DISCUSSION

A. General Characteristics

To observe the decrease in apparent viscosity with time of shearing, the change in shearing stress with time while shearing the oil at a constant rate was recorded. Typical stress-time curves for a number of shear rates at -30° C are shown in Figure 74. At the higher rates of shear the stress-time curves may be approximately represented as an exponential relaxation equation,

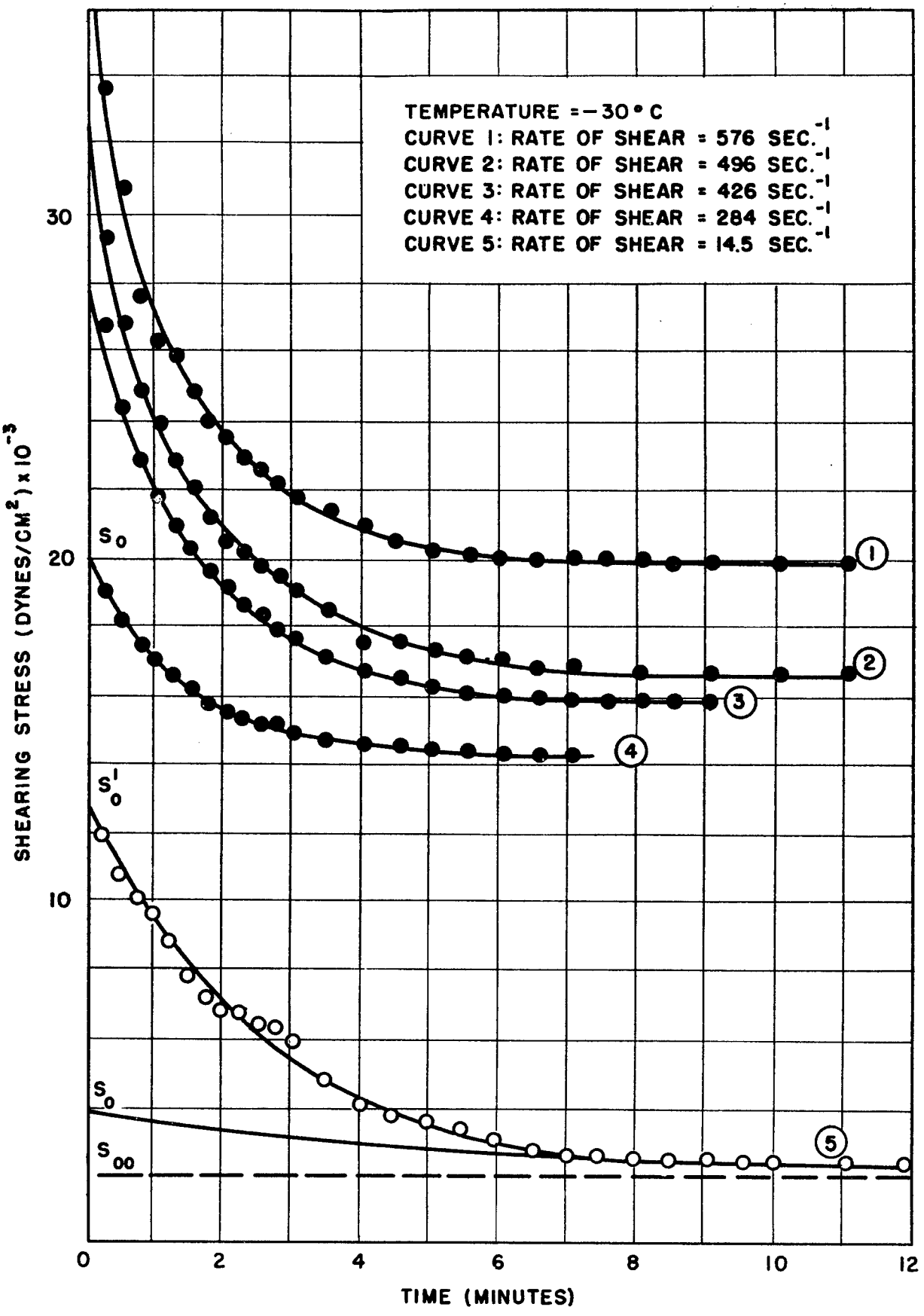


FIG. 74 - STRESS RELAXATION CURVES AT CONSTANT RATES OF SHEAR.

$$(3) \qquad S_t = (S_o - S_\infty)\, e^{-t/t_r} + S_\infty$$

where the shearing stress, S_t, decreases as a function of time, t, from an initial value, S_o, to an equilibrium value, S_∞, at a rate determined by the relaxation time, t_r.

At very low rates of shear, however, such as curve 5, Figure 74, the stress-time curves exhibit a marked deviation from equation (1) and it becomes necessary to add higher order terms to approximate the form of the curves. Two exponential terms of a series is a reasonably good approximation of the data, thus:

$$(4) \qquad S_t = (S_o - S_\infty)\, e^{-t/t_r} + (S_o' - S_o)\, e^{-t/t_r'} + S_\infty .$$

In Figure 75 the stress-time data at a number of constant rates of shear have been used to construct the consistency curves for the oil initially, i.e., at zero time, and when the rigid structure is completely reduced, S_∞. This reveals that the initial stress at low shear rates, S_o', is disproportionately higher than for high shear rates, S_o. The explanation becomes apparent from the calculated values of relaxation times, t_r and t_r', in Figure 76, showing that the higher order terms become rapidly transient with increasing rates of shear and would not be observed experimentally. Thus, while the consistency of the unsheared oil would appear to correspond with the S_o curve in Figure 75 on the basis of experiments at high rates of shear, it must at least be as high as S_o', which curve is largely undetermined, the breakdown in the initial structure being very rapid at high shear rates.

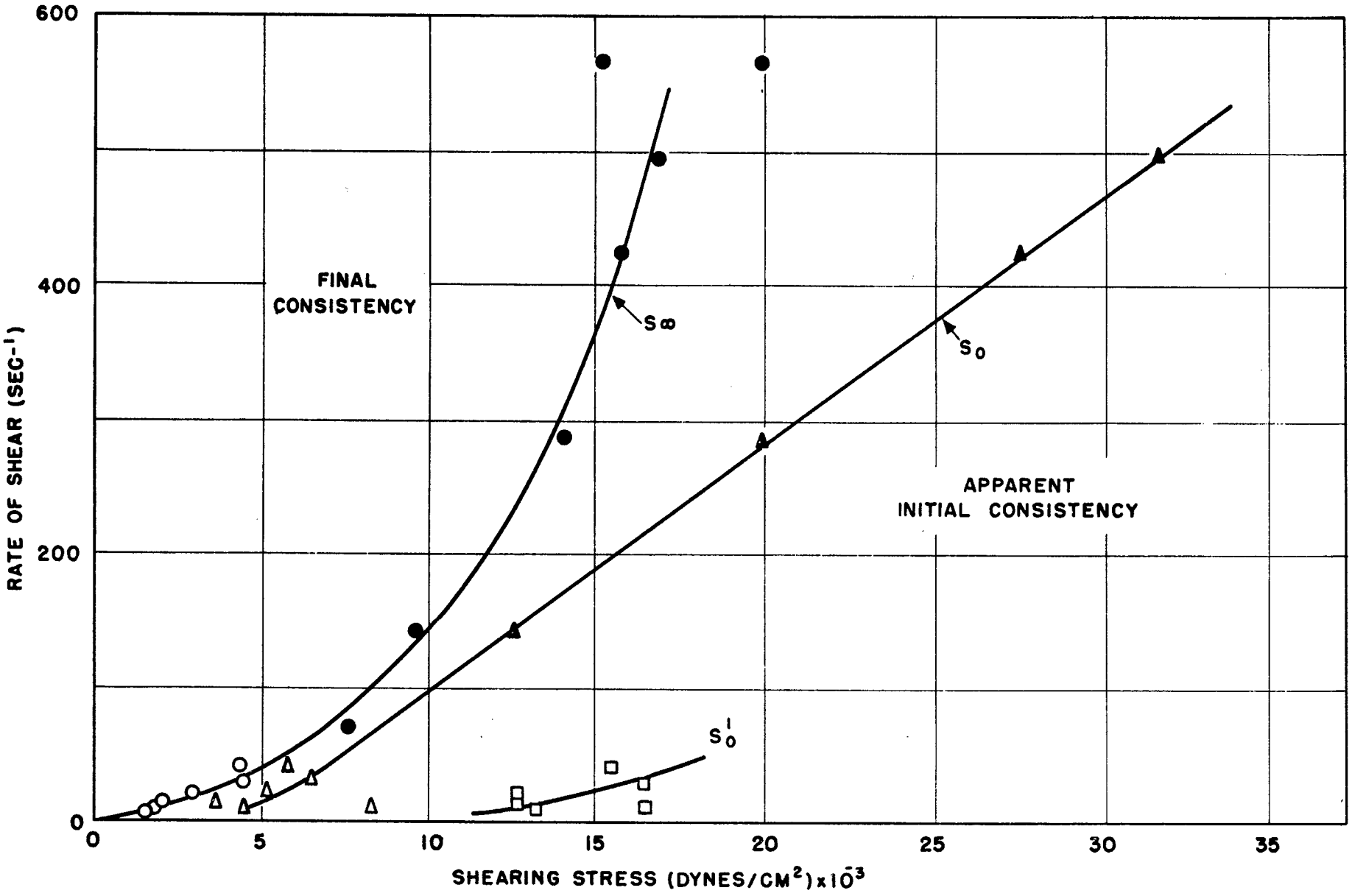


FIG. 75 - CONSISTENCY CURVES FOR PENN. 150 NEUTRAL OIL CONSTRUCTED FROM STRESS RELAXATION DATA.
TEMPERATURE = -30°C

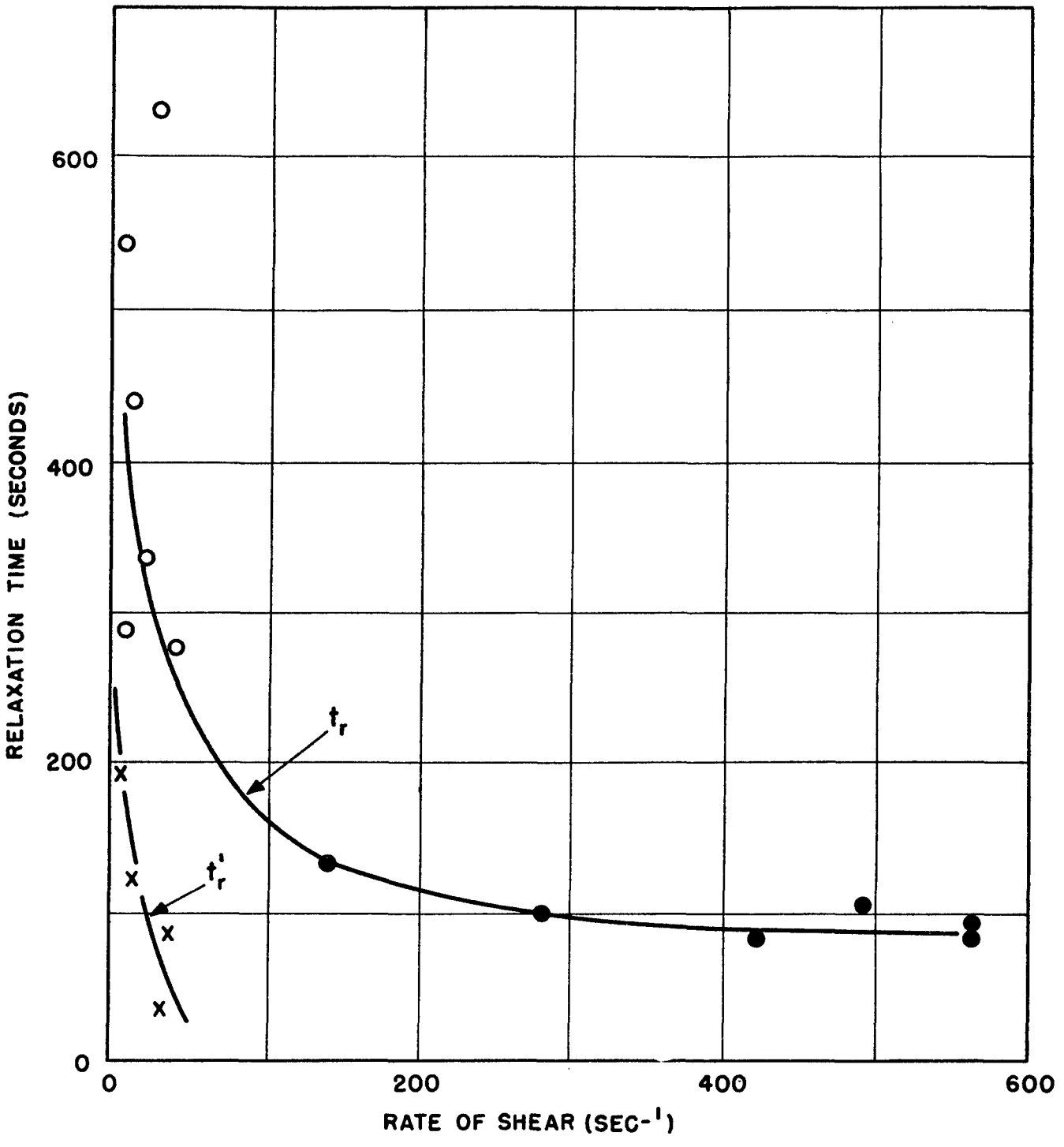


FIG. 76 - RELAXATION TIMES AS A FUNCTION OF RATE OF SHEAR
TEMPERATURE = -30°C

Stress relaxation curves from experiments employing a much lower cooling rate permitting a higher degree of crystallinity are shown in Figure 77. Here it is quite evident that a rapid degeneration of structure occurs in the first seconds of shearing and that the initial stress is quite high and impossible to determine by extrapolation. Cooling rate was observed to have no effect on equilibrium stress, as may be seen in Figure 82 to be presented later in the text.

At equilibrium the shearing stress for corresponding rates of shear describes the S_∞ curve in Figure 75, however, this curve is not uniquely defined, and the experiment depicted in Figure 78 demonstrates that the oil in this state is essentially a Newtonian liquid with an equilibrium viscosity which decreases with increasing rates of shear. If the oil is sheared until equilibrium is attained at some constant shear rate, $\dot{e}_1$, a consistency curve then determined in a time short compared to the relaxation time, t_r, is linear through the origin. Increasing the rate of shear to a higher level, $\dot{e}_2$, results in an initial stress, S_2, followed by a relaxation to S_3, corresponding to an equilibrium Newtonian viscosity for the higher rate of shear. The departure from linearity of the curves from higher rates of shear may be attributed to relaxation during the time required for the determination.

In the matter of a recovery in viscosity when the oil is allowed to "rest" after shearing to equilibrium the behaviors at high and low rates of shear are in marked contrast. Viscosities computed from rapidly determined consistency curves after successive 5-minute intervals of no shearing, following shearing to equilibrium at 496 sec^{-1}, show a rapid increase

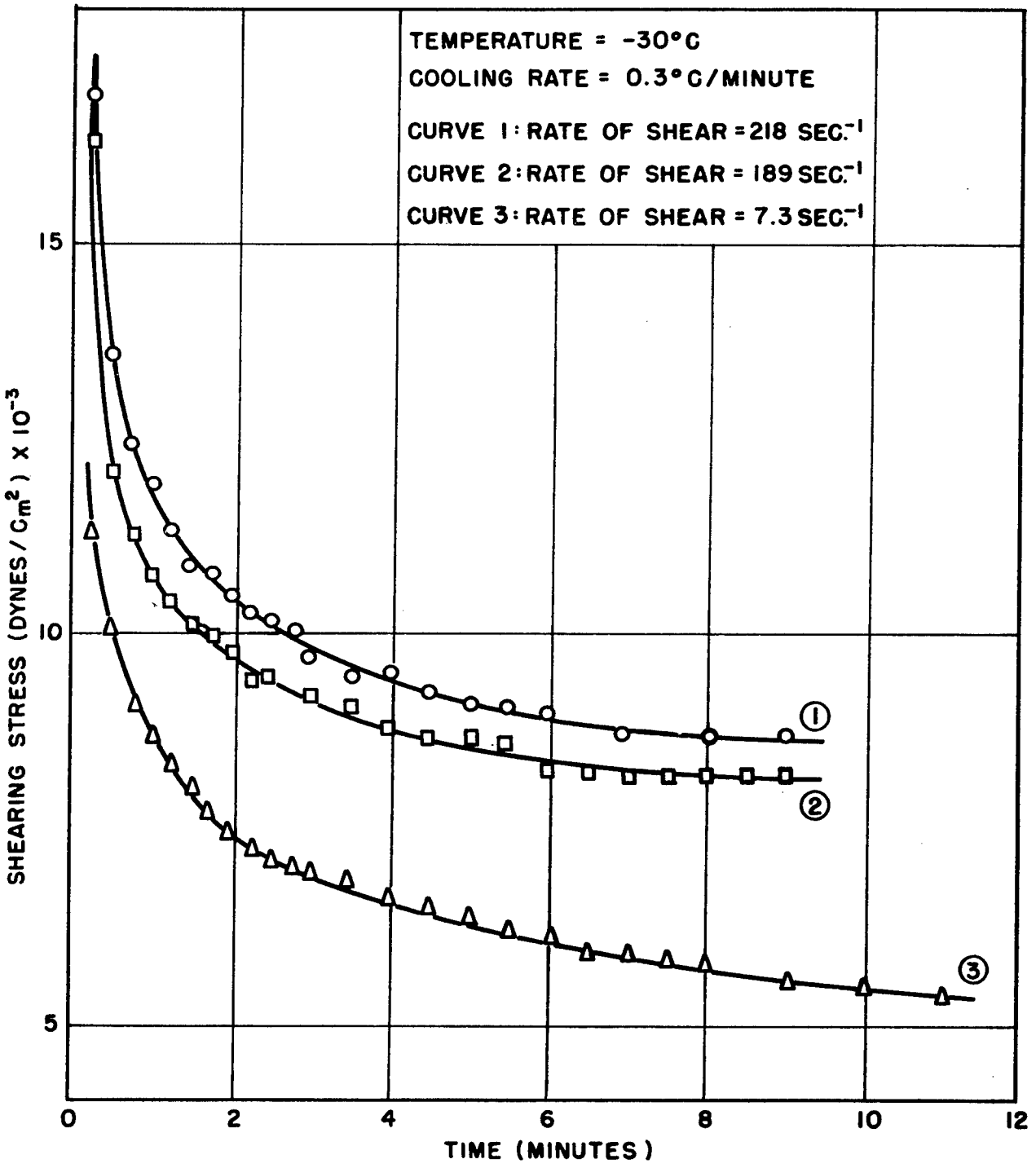


FIG. 77 - STRESS RELAXATION CURVES FOR A LOW RATE OF COOLING

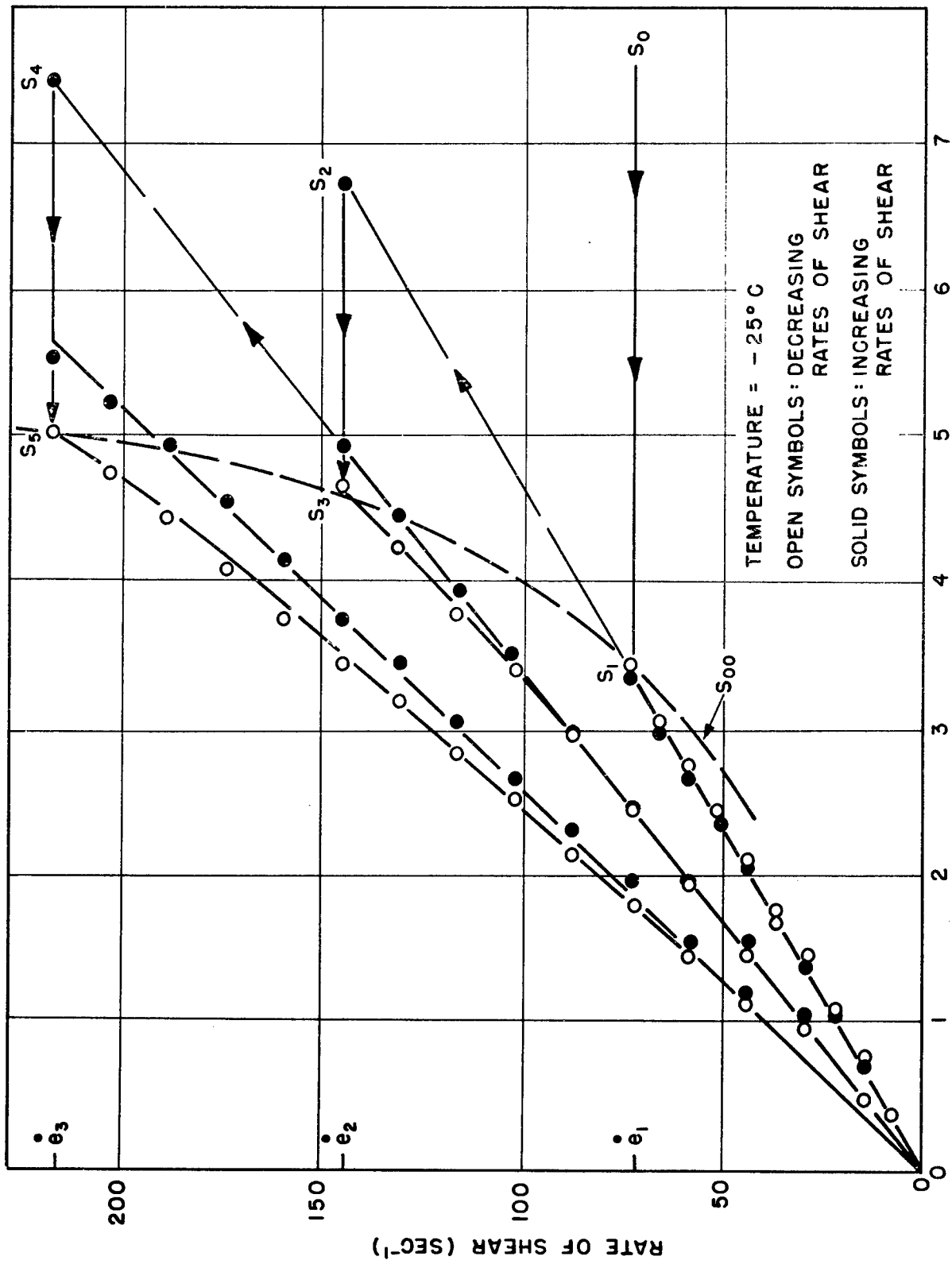


FIG. 78 — CONSISTENCY CURVES DETERMINED AFTER REACHING EQUILIBRIUM AT SUCCESSIVELY HIGHER RATES OF SHEAR.

(Figure 79). On the other hand, no increase in viscosity was observed after two hours rest when a sample had been sheared to equilibrium at 14.5 sec^{-1} (Figure 80).

The differences in behavior observed at low and high shear rates may be reconciled if it is concluded that two different phenomena are involved, namely, (1) an irreversible (within the time scale of the experiment) breakdown in the initial rigid structure of the oil, which is predominant at low shear rates and rapidly transient at high rates of shear, and (2) a reversible apparent thixotropy predominant at high rates of shear and similar to the behavior of high viscosity oils at room temperature reported by Weltmann[25][26].

Weltmann attributed the apparent thixotropy of high viscosity oils in a rotational viscometer to molecular orientation in the main, however, temperature effects due to heat generated in shearing are known to play some part in the decrease in viscosity as evidenced by recorded rises in temperature at the bob wall. The temperature rise was found to be proportional to the cup to bob clearance[26]. If temperature effects contribute to the observed decrease in viscosity with increased rate of shear the equilibrium viscosity should show a dependence on cup to bob clearance. Such a dependence was observed, the equilibrium viscosities being consistently higher when measured with a 1.4 cm cup than with a 1.5 cm cup, giving clearances of 1.0 mm and 2.0 mm, respectively.

B. Temperature Effects

The effect of frictional heating on the measured value of the equilibrium viscosity can be calculated from the equations of heat flow

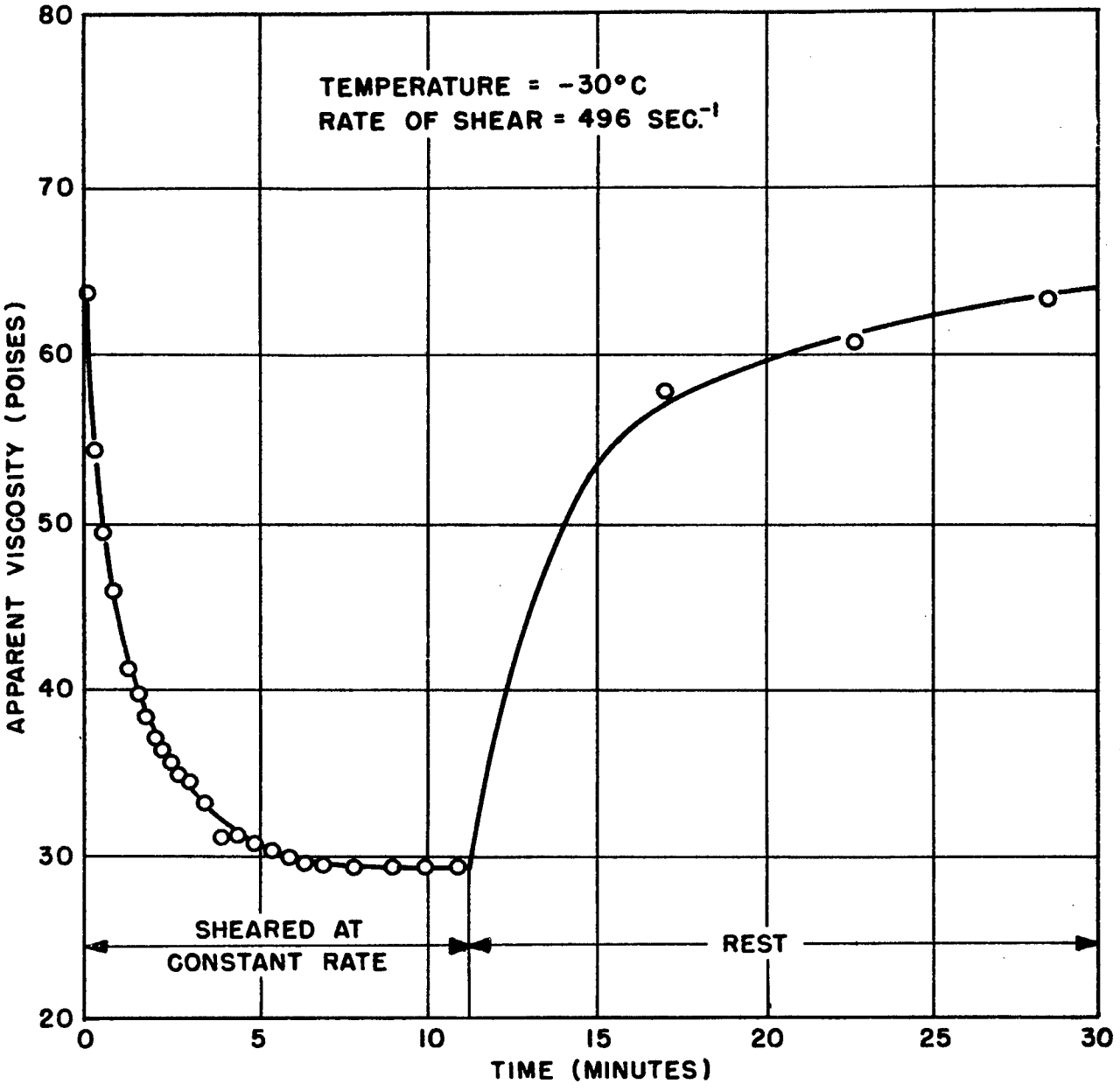


FIG. 79 – RECOVERY OF VISCOSITY ON STANDING AFTER SHEARING TO EQUILIBRIUM AT A HIGH RATE OF SHEAR.

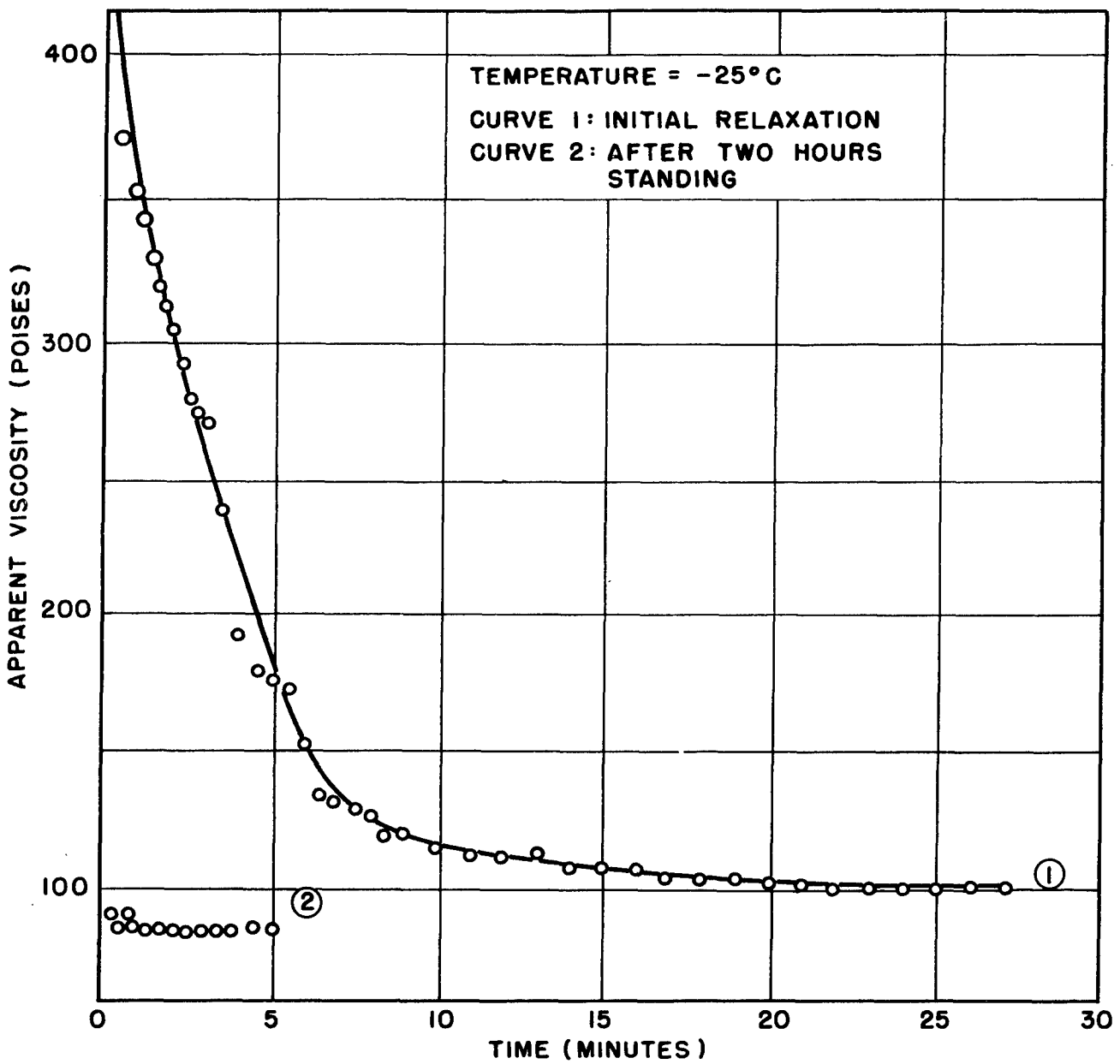


FIG. 80 - RELAXATION CURVES DETERMINED AT A LOW RATE OF SHEAR INITIALLY AND AFTER TWO HOURS STANDING.

and mechanical equilibrium if the flow is assumed to be Newtonian. Since the cup to bob clearance is small compared to the cup radius, it is a sufficiently good approximation to treat the case of plane flow. This has been done by Hagg[27] for a number of cases corresponding to assumed temperatures at the cup and bob. The temperature dependence of viscosity was assumed to have the form:

$$(5) \qquad \eta(T) = \eta_o e^{-\alpha T}$$

where η_o is the viscosity at the reference temperature (the cup temperature in the present case), T is the temperature rise, and α the temperature coefficient of viscosity. For the case at hand, it is assumed that the cup temperature is maintained at the temperature of the bath and that the bob is thermally insulated. The calculation then gives for the temperature rise of the bob at thermal equilibrium the result:

$$(6) \qquad T_{bob} = (1/\alpha)\ln(1 + \beta/2),$$

where β is a dimensionless parameter given by the alternative forms:

$$(7) \qquad \beta = \frac{\alpha \eta_o R_c \omega^2}{\mathcal{K}} = \frac{\alpha \eta_o d^2}{\mathcal{K}} \left(1 + \frac{d}{R_b}\right) \dot{e}^2 ,$$

the other symbols being defined as follows:

R_b = radius of the bob,

R_c = radius of the cup

$d = R_c - R_b$ = cup-to-bob clearance

ω = angular velocity of the cup

$\dot{e}$ = rate of shear

$\mathcal{K}$ = thermal conductivity of the oil.

Calculation of the apparent viscosity at thermal equilibrium yields the result:

$$(8) \qquad \eta = \eta_o \sqrt{\frac{2}{\beta}} \quad \frac{\sinh^{-1} \sqrt{\beta/2}}{\sqrt{1 + \beta/2}}$$

In order to estimate the possible magnitude of the viscosity change due to the rise in temperature of the oil, it is assumed that the completely sheared oil is a Newtonian liquid and that the dependence of equilibrium viscosity on rate of shear is due entirely to heating effects. The true viscosity, η_o, can then be estimated from the slope at the origin of the S_∞ curve (Figure 81). This gives 90 poises and 220 poises for η_o at -25° C and -30° C, respectively, from which the viscosity-temperature coefficient at -30° C is found:

$$\alpha = \frac{\ln 220 - \ln 90}{5} = .18 \ (°C)^{-1} \ .$$

The thermal conductivity is taken to be:

$$\mathcal{K} = .00035 \text{ cal/cm - sec - °C} = 1.5 \times 10^4 \text{ ergs/cm - sec - °C.}$$

Expressed in terms of the rate of shear, $\dot{e}$, as defined by equation (2), β is given by

$$(9) \qquad \beta = \frac{\alpha \eta_o d^2}{\mathcal{K}} \left(1 + \frac{d}{R_b}\right) \dot{e}^2 \ .$$

At a rate of shear of 600 sec^{-1} the temperature rise of the bob is calculated to be 10° C and 17° C for the 1.4 cm and 1.5 cm cups, respectively. With such high temperature rises it appears unlikely that the assumption that the bob is thermally insulated is a good approximation. If account were taken of the heat loss of the bob to the surroundings the

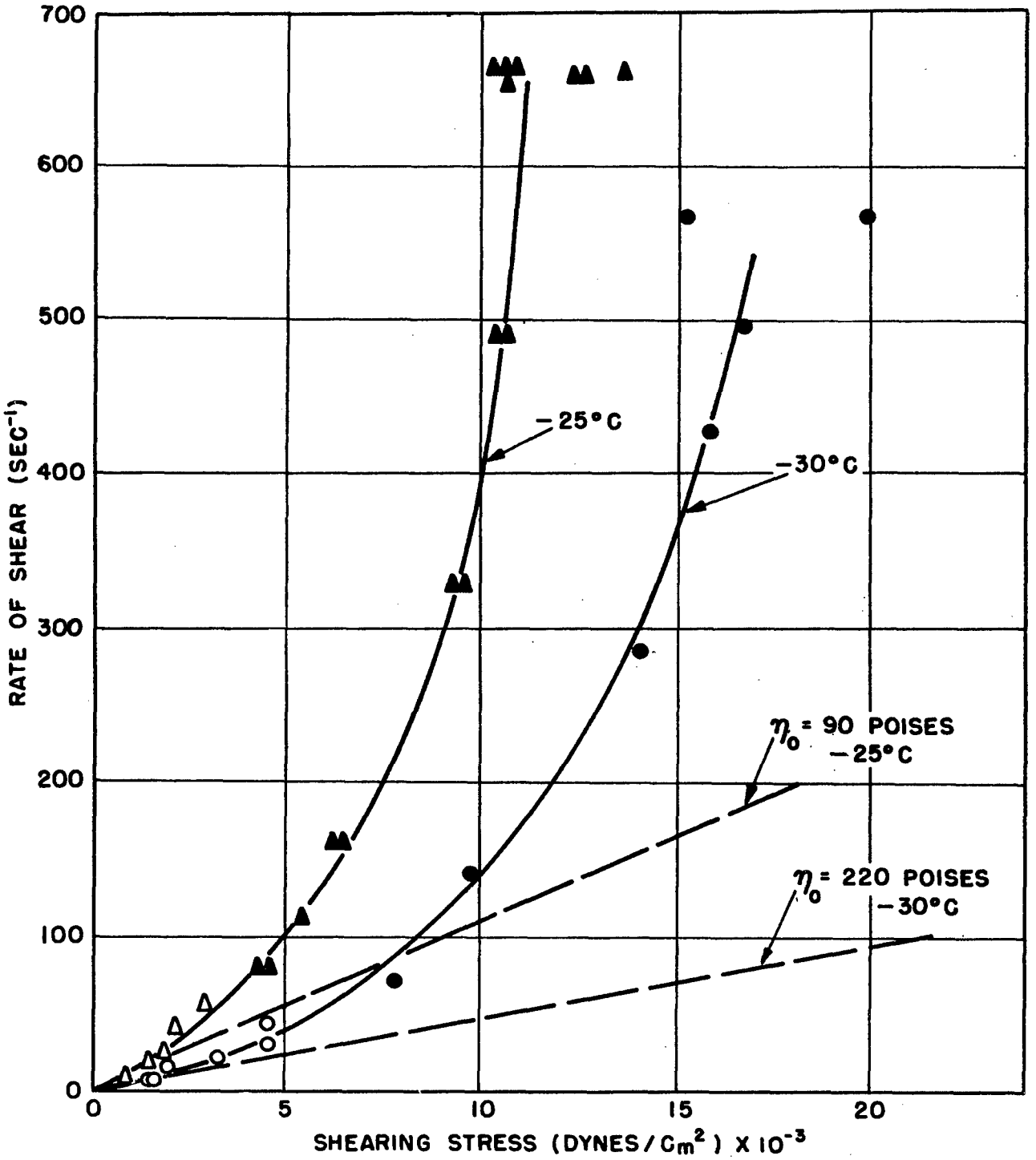


FIG. 81 – ESTIMATED EQUILIBRIUM VISCOSITIES IN THE LIMIT OF LOW RATES OF SHEAR AT -25°C AND -30°C

calculated equilibrium viscosities would not fall off as rapidly with increasing rate of shear.

A comparison of the calculated and observed equilibrium viscosities appears in Figure 82. Heating effects are of the correct order of magnitude and in qualitative agreement with the observations, although the viscosity falls off much more rapidly than predicted from the calculations. A possible source of discrepancy, in addition to the assumed perfect thermal isolation of the bob, is the uncertainty in the choice of the initial viscosity, η_0, and likewise in the determination of the temperature coefficient, α, used in the theoretical formula. In any event, it appears that heating effects do not explain the entire relaxation of viscosity to the equilibrium value.

C. Wax-Oil Suspensions

The existence of a network of solid wax crystals in natural petroleum oils below their pour points has been reported by Erk[21], who suggests that this structure is responsible for the rigidity. In order to determine the effect of suspended wax in an oil under such conditions that temperature effects may be neglected, a study was made of the rheology of Pennsylvania 150 Neutral oil containing seven per cent n-octacosane. Observations were made at +30° C using a modified Stormer viscometer with which very low rates of shear may be obtained.

With the Stormer viscometer the amount of continuous shearing possible without rewinding the line to which the load is attached is about 100 revolutions. When the sample is sheared to this extent repeatedly at constant load the breakdown is additive and with the same result as if the

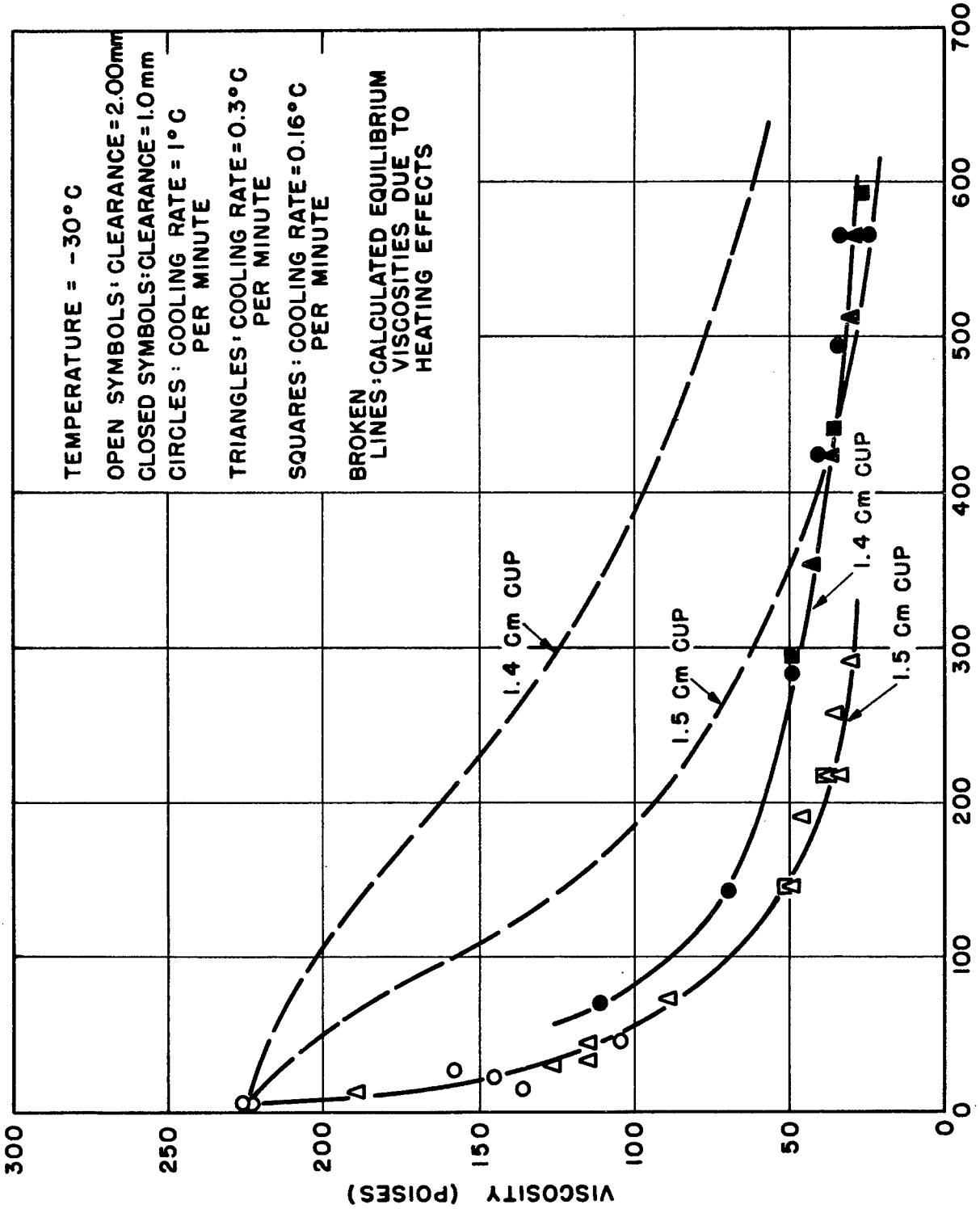


FIG. 82 - CALCULATED AND OBSERVED EQUILIBRIUM VISCOSITIES FOR TWO CUP TO BOB CLEARANCES.

sample had been sheared continuously for the same number of revolutions. Furthermore, when different loads are used the increase in fluidity of the sample is a function of the total work which has gone into shearing, i.e., the sum of the products of the load and the number of revolutions of the viscometer at that load. Data obtained from a single experiment are shown in Figure 83, where the rate of shear at constant loads is plotted against the total work of shearing. The shearing was not continuous and was with shearing stresses varying from 65 to 177 dynes/cm^2. The same data are used to plot the consistency curves for the suspension at different degrees of breakdown in Figure 84, which shows a progression from plastic flow to Newtonian flow with a continuously decreasing viscosity toward a minimum. The discontinuities appearing in the curves in Figure 83 are not clearly understood, but are attributed to changes due to fluctuations in temperature of the sample.

Since the degree of breakdown is determined by the work done in shearing, the rate of relaxation at constant rates of shear should be determined by the rate of energy input to the system. Thus, as a first approximation, the relaxation times should be inversely proportional to the square of the rate of shear, which is in accord with the rapid decrease in relaxation times observed for the natural oil at low temperatures.

In the case of Pennsylvania 150 Neutral oil and the high pour point mixture containing suspended n-octacosane, the failure to exhibit recovery of rigidity after shearing and the Newtonian flow characteristics of the sheared samples in all but the very early stages of breakdown suggest that the forces of adhesion between the wax crystals are not the

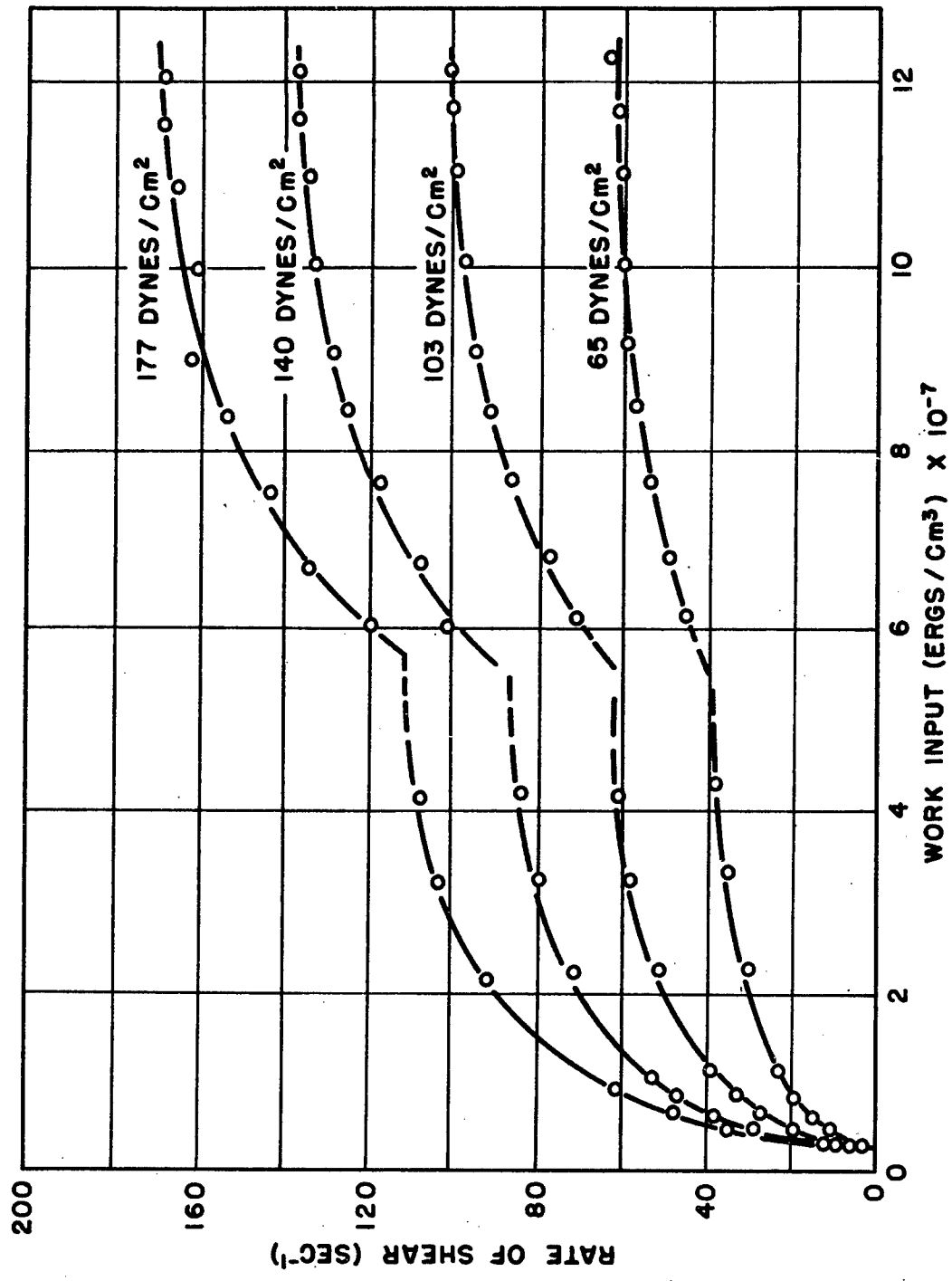
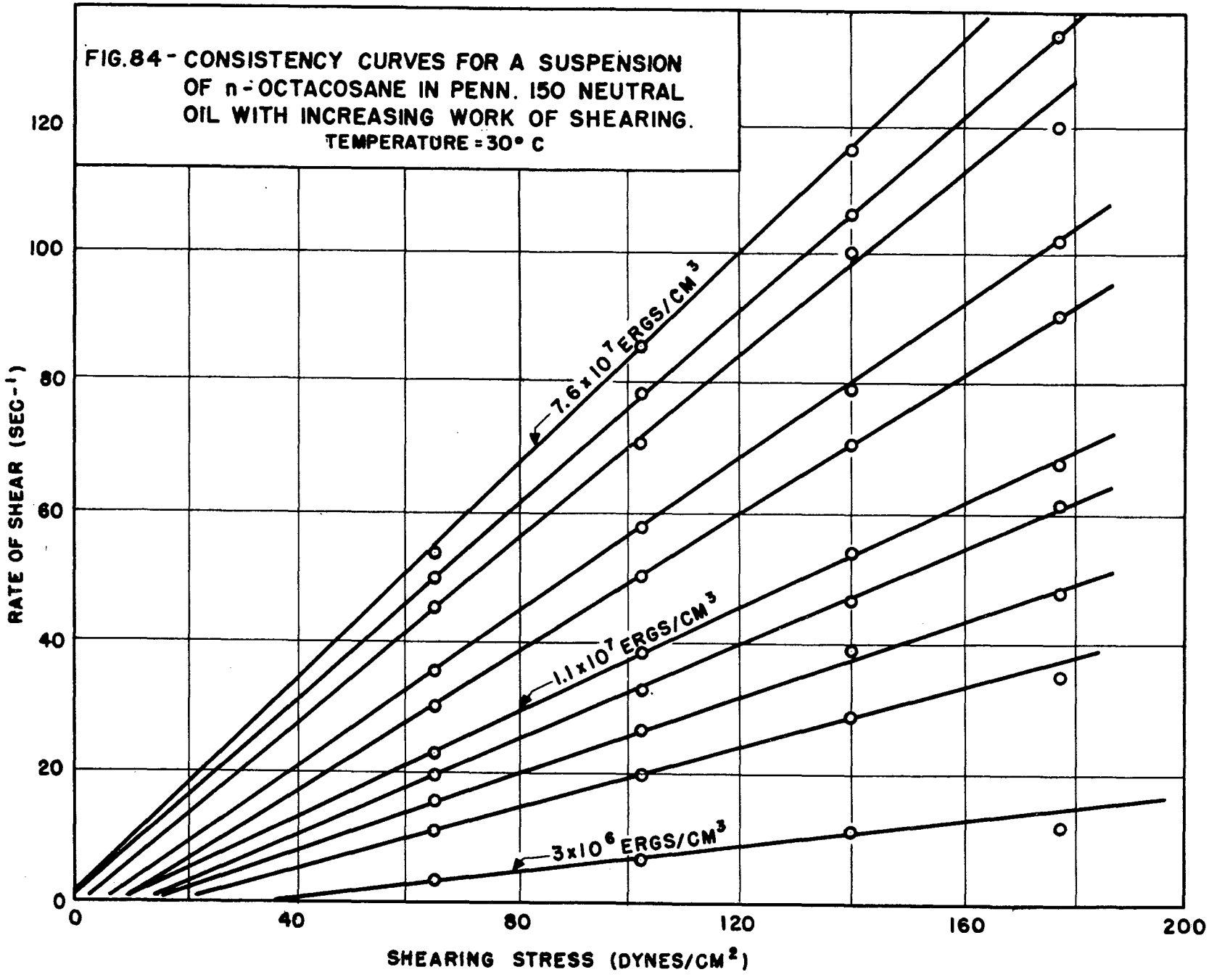


FIG. 83 – THIXOTROPY OF A SUSPENSION OF N-OCTACOSANE IN PENNSYLVANIA 150 NEUTRAL OIL AT CONSTANT SHEARING STRESSES. (TEMPERATURE = 30°C)


FIG. 84 - CONSISTENCY CURVES FOR A SUSPENSION OF n-OCTACOSANE IN PENN. 150 NEUTRAL OIL WITH INCREASING WORK OF SHEARING.
TEMPERATURE = 30° C
RATE OF SHEAR (SEC⁻¹)
SHEARING STRESS (DYNES/CM²)
0
20
40
60
80
100
120
0
40
80
120
160
200
7.6 x 10⁷ ERGS/CM³
1.1 x 10⁷ ERGS/CM³
3 x 10⁶ ERGS/CM³

electrical forces attributed to normal gels. The observed properties may be explained by assuming that the adhesion is through lattice forces, i.e., that the crystals are grown together, and that the decreasing viscosity is due to the mechanical degradation of this rigid network into progressively smaller units due to shearing.

4. CONCLUSIONS

The thixotropy exhibited by Pennsylvania 150 Neutral oil below its pour point in a rotational, concentric-cylinder viscometer may be resolved into two processes occurring simultaneously:

1. A degeneration of the rigid structure, predominantly observed at low rates of shear and occurring very rapidly at high rates of shear.

2. A reversible apparent thixotropy occurring predominantly at high rates of shear.

A calculation of the form and magnitude of temperature effects due to frictional heating accounts for a large part but not all of the latter effect.

A suspension of a pure normal paraffin hydrocarbon precipitated in a petroleum oil produces a high pour point system which has been studied in the absence of heating effects. This system exhibits a progressive increase in fluidity as a function of the work done in shearing, and a transition from plastic to Newtonian flow.

An explanation proposed is that the wax crystals existing in the saturated solution are grown together at the points of contact and that this matrix is mechanically degraded due to shearing.

5. APPENDIX OF MANUSCRIPT

Temperature Effects in the Measurement of Viscosity with the Rotational Viscometer

For the case of a rotational, concentric-cylinder viscometer the effect of frictional heating on the measured value of viscosity can be calculated from the equations of heat flow and mechanical equilibrium if the flow is assumed to be Newtonian. This analysis has been carried out and given in an earlier report[28] for an assumed viscosity-temperature law of the form:

$$(1) \qquad \eta = \frac{\eta_0}{1 + \alpha T}$$

In the present case the solution is given assuming the more realistic temperature dependence of viscosity given by,

$$(2) \qquad \eta(T) = \eta_0 e^{-\alpha T} ,$$

η_0 being the viscosity at the reference temperature and $\eta(T)$ the viscosity for any temperature rise, T. The constant, α, is the temperature coefficient of viscosity.

The solution to this problem for a number of boundary conditions has been given by Hagg[27] for the case of frictional heating in journal bearings. The results obtained here for the rotational viscometer, when reduced to the same terms, are in agreement with Hagg.

This analysis was made for the Precision-Interchemical viscometer in which the cup turns and the inner cylinder is stationary, although it is unimportant whether the inner or outer cylinder rotates. Since the cup

to bob clearance is small compared to the cup radius, it is a sufficiently good approximation to trest the case of plane flow. Denoting the temperature rise of the oil by T and the coordinate in the radial direction, measured from bob to cup, by x, the equation for heat flow becomes

$$(3) \qquad \kappa \frac{d^2T}{dx^2} = -\eta(T) \left(\frac{dV}{dx}\right)^2$$

where

κ = thermal conductivity of the oil.

$\eta(T)$ = viscosity as a function of temperature.

$V(x)$ = linear velocity of the cup.

The term on the right side represents the generation of heat per unit volume due to viscous friction.

If it is assumed that the cup temperature is maintained at the temperature of the bath and that the bob is thermally insulated, the boundary conditions become

$$(4) \qquad \frac{\partial T}{\partial x}(0) = 0$$

$$T(d) = 0,$$

where d is the cup to bob clearance. The equation for mechanical equilibrium is

$$(5) \qquad \frac{d}{dx}\left[\eta(T)\frac{dV}{dx}\right] = 0,$$

with the boundary conditions

$$(6) \qquad V(0) = 0$$

$$V(d) = R_c \omega,$$

R_c being the radius of the cup and ω its angular velocity.

With the temperature dependent viscosity, $\eta(T)$, given by equation (2), where η_o is the temperature of the cup which is assumed to be the same as the viscometer bath, the solution to this system of equations gives the following result for the temperature distribution across the annular space at thermal equilibrium:

$$(7) \qquad T(x) = \frac{1}{\alpha} \ln \left[(1 + \beta/2) \operatorname{sech}^2 \left(\frac{x}{d} \sinh^{-1} \sqrt{\beta/2} \right) \right],$$

where β is a dimensionless parameter given by,

$$(8) \qquad \beta = \frac{\alpha \eta_o R_c^2 \omega^2}{\kappa}$$

The maximum temperature rise occurs at the bob, and is given by,

$$(9) \qquad T(0) = \frac{1}{\alpha} \ln (1 + \beta/2)$$

The apparent viscosity at thermal equilibrium is given by,

$$(10) \qquad \eta = \eta_o \sqrt{2/\beta} \; \frac{\sinh^{-1} \sqrt{\beta/2}}{\sqrt{1 + \beta/2}}$$

Equations (9) and (10) give the temperature rise at the bob and apparent viscosity, respectively, at thermal equilibrium. The problem of the transient behavior, or time dependence of viscosity is considerably more difficult, however, the relaxation time may be estimated from the time constant for thermal equilibrium. For this purpose the temperature dependence of viscosity is neglected, a good approximation only at low rates of shear. The heat flow equation in this case becomes

$$(11) \qquad \kappa \frac{\partial^2 T}{\partial x^2} = -\eta_o \left(\frac{\partial V}{\partial x} \right)^2 + \rho c \frac{\partial T}{\partial t}$$

where ρ is the density of the oil and c is its specific heat. The boundary condition at x = 0 now becomes

$$(12) \qquad 2\pi R_b h \varkappa \frac{\partial T}{\partial x}(0) = \pi R_b^2 h \rho_b C_b \frac{\partial T}{\partial t}(0)$$

where ρ_b and C_b are the density and specific heat of the bob, respectively, R_b is the bob radius and h its height. The transient temperature will be a sum of terms of the form

$$(13) \qquad T(x,t) = A_\tau \sin \sqrt{\frac{\rho c}{\varkappa \tau}}\,(d-x) e^{-t/\tau},$$

where the coefficients A_τ are determined by the initial temperature distribution. The boundary condition at x = 0 imposes the following equation for τ:

$$(14) \qquad \sqrt{\frac{\rho c}{\varkappa \tau}} \cdot d \tan \frac{\rho c}{\varkappa \tau} \cdot d = \frac{2 \rho c d}{\rho_b C_b R_b} .$$

Using the numerical values:

$$\rho = 0.9 \text{ gms/cm}^3$$
$$c = 0.45 \text{ cal/gm °C}$$
$$\rho_b = 7.83 \text{ gms/cm}^3$$
$$C_b = 0.11 \text{ cal/gm °C}$$
$$d = 0.2 \text{ cm}$$
$$R_b = 1.3 \text{ cm},$$

the right hand side takes the value 0.144. To calculate the principal root for such a small value the tangent function may be replaced by its argument and the equation solved directly for τ, yielding the result:

$$(15) \qquad \tau = \frac{\rho_b C_b R_b d}{2 \varkappa}$$

With the numerical values given above, τ = 320 seconds, which applies to the 1.5 cm cup, or 160 seconds for the 1.4 cm cup. In Figure 76 it is shown that the relaxation times for viscosity at rates of shear above 100 sec^{-1}, where the reversible thixotropic effect can be separated from the irreversible breakdown effect, were about 100 sec. for the 1.4 cm cup. In view of the assumptions made in these calculations, this is considered sufficiently close agreement that the effect can be attributed to frictional heating.

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$$(11) \qquad \kappa \frac{\partial^2 T}{\partial x^2} = - \eta_o \left(\frac{\partial V}{\partial x} \right)^2 + \rho c \frac{\partial T}{\partial t}$$