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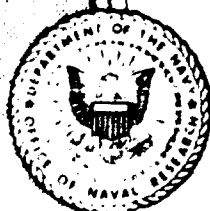
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WATER-DISPLACING FLUIDS AND THEIR APPLICATION TO RECONDITIONING AND PROTECTING EQUIPMENT

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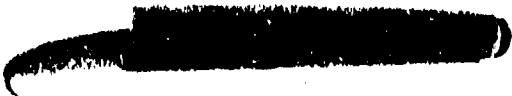
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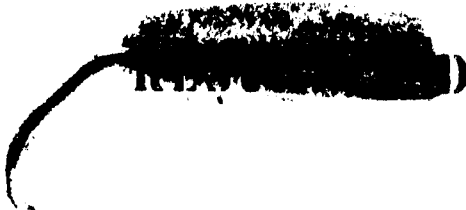


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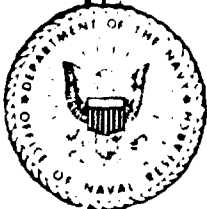
**WATER-DISPLACING FLUIDS AND THEIR APPLICATION
TO RECONDITIONING AND PROTECTING EQUIPMENT**

H. R. Baker and W. A. Zisman

October 4, 1948

Approved by:

Dr. P. Borgstrom, Superintendent, Chemistry Division



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CONTENTS

Abstract	iv
Problem Status	iv
Authorization	iv
I. INTRODUCTION	1
II. THEORETICAL ASPECTS	2
A. The Problem of Rust Inhibition	2
B. The Volatile Solvent as Major Component	2
C. Importance of the Equilibrium Spreading Pressure	3
D. Water Solubility vs. Preferential Wetting of Metals	7
E. Requirements for Optimum Properties	7
III. DEVELOPMENT OF HIGHLY EFFECTIVE FLUIDS	10
A. Relation of Molecular Structure of Volatile Liquids to Equilibrium Spreading Pressure	10
B. Preferential Wetting and Water-Displacing Ability	21
C. Polar Compounds for Rust-Inhibiting Solutes	26
D. Consideration of Effects on Plastics	27
E. Storage of Fluids and Antioxidants	28
F. Some Promising Compositions	30
IV. LABORATORY EVALUATION OF WATER-DISPLACING FLUIDS	30
A. Effectiveness of One-Drop Test	30
B. Further Tests on Rust Preventive Properties	33
C. Tests on Water-Soaked Electric Motor-Generators	37
D. Discussion of Commercially Available Fluids	39
V. SUMMARY	42
VI. RECOMMENDATIONS	42
VII. ACKNOWLEDGMENT	42

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ABSTRACT

A fundamental investigation was made of organic fluids able to displace thin layers of water from metals by a preferential wetting mechanism. The preferred fluids of this class are combined with small concentrations of rust inhibitors of the polar type in order to improve protective and rust-preventive properties. Finally, addition of traces of antioxidants is shown to be effective in giving an increased storage stability to the fluids.

Comparisons are given of the new fluids with the commercially available materials. Applications to the reconditioning of electric motors, generators, and starters are described, and a variety of other military and industrial uses are indicated. Some of the most promising of the new compositions are recommended for service tests.

PROBLEM STATUS

This is an interim report; further work is contemplated in cooperation with interested Bureau activities.

AUTHORIZATION

NRL Problem No. C02-01R (BuShips Project No. 414/46).

WATER-DISPLACING FLUIDS AND THEIR APPLICATION TO RECONDITIONING AND PROTECTING EQUIPMENT

I. INTRODUCTION

After compartments within ships have been flooded, it is often necessary to replace or recondition water-soaked equipment. At the present time the reconditioning is done by using the materials and methods described in Bureau of Ships Circular Letter No. 9a dated 14 September 1944 and entitled "Instructions for Reconditioning Electrical Equipment which has been Submerged in Sea Water." The rapid restoration of the equipment to operability at least for a short time is a minimum requirement to care for naval emergencies. The ultimate goal, however, is a simple procedure which would permit a permanent restoration of equipment. It is particularly desirable to be able to recondition flooded equipment without dismounting or dismantling it.

The present reconditioning method involves (a) displacing the sea water and the soluble salts contained therein by flushing with tap water (or distilled water), (b) displacing the tap water from the surface of the metal and nonmetallic parts of the electrical equipment by a noninjurious fluid, and (c) treating the metal parts to prevent further corrosion without injuring the electrical performance. Experience has shown that success in preventing corrosion depends upon complete removal of the salts and upon promptness in applying the rust preventive after removal of the equipment from the water.

A similar but simpler problem is encountered when torpedoes are given trial runs. After each run the torpedo is hauled out of the sea, whereupon a quick treatment with a water-displacing compound and rust inhibitor is advantageous in preventing rusting. The material used is one of a number of commercial preparations made to conform to Navy Department Specification 52-C-18.

The present electrical practice, described in the above referenced Circular Letter No. 9a, involves the use of Navy Specification 52-C-18 Grade III Compound, Rust Preventive, Thin Film (Polar Type). The commercial materials supplied under this specification have been reported to be variable in performance. They are often toxic, they are very flammable (flash point specified not less than 100°F), they often seriously attack paint and varnish, and they may leave tape and fabric insulation soggy and sticky—faults due largely

to the aromatic hydrocarbon fraction in the petroleum solvents or diluents commonly used.

In this investigation a fundamental study has been made of the mechanism of action of water-displacing fluids, and thereafter it was attempted to develop a number of improved fluids suitable for electrical and mechanical use. Finally, applications have been made on a laboratory scale to the reconditioning of several electrical motors which had been submerged in synthetic sea water.

II. THEORETICAL ASPECTS

A. The Problem of Rust Inhibition

The surface of a metal can be protected from water by a coating of a water-repellent film. Although coatings of hydrocarbon waxes or fluids are water repellent, they do not adhere long because the water eventually displaces them to wet the metal preferentially. If certain types of high-molecular-weight polar compounds are added to the wax or fluid, this displacement by water cannot occur. Research in this Laboratory^{1,2,3} has demonstrated the effectiveness of these films in inhibiting corrosion and has shown that the inhibition is due to the formation of an adsorbed and oriented film which is usually only one molecule thick. The physical and colloidal chemistry of adsorptive and protective mechanisms involved was given a fundamental and careful treatment for the first time, and a thorough study was made of the relation between organic structure and the rust inhibiting property.

B. The Volatile Solvent as Major Component

For the applications concerned here, polar rust inhibitors must be capable of being brushed or sprayed on the previously submerged equipment. But most of the effective polar rust inhibitors are either solids or high-boiling, viscous liquids. And for the further reason that greasy or oily residual coatings are undesirable, the polar inhibitor must be dissolved or dispersed in a less viscous solvent. Since a monolayer is responsible for the water-displacing property, it is only wasteful to use more additive than necessary to form a monomolecular film on the metal surface. Indeed, when larger quantities are used, a tacky or waxy coating remains after evaporation of the solvent. And while this film may increase the resistance of the metal to prolonged or severe exposure, it may also be undesirable otherwise. In any case, the use of a volatile solvent tends to lower the cost of the treatment.

An objective of this research has been to show how to select the most suitable from among the many available polar-type rust inhibitors. Of course,

¹ H. R. Baker and W. A. Zisman, "Anti-Rust Additives for Lubricating, Power Transmission, and Protective Oils," NRL Report No. P-2474, February 1945.

² H. R. Baker and W. A. Zisman, Ind. Eng. Chem., 40, pp. 2338-2347, (1948).

³ H. R. Baker, D. T. Jones, and W. A. Zisman, Ind. Eng. Chem., in press.

the inhibitor must be cheap; it must be high-boiling, nontoxic and non-corrosive to copper, brass, iron, and aluminum. It must be sufficiently soluble in the organic thinner or solvent. And finally it must be as harmless as possible to the common electrical insulating materials.

Obvious requirements for the ideal solvent or diluent are: (a) high flash point; (b) boiling point low enough for sufficiently rapid evaporation; (c) low cost; (d) nontoxicity; (e) little or no attack on common electrical insulating materials; and (f) noncorrosiveness to iron, copper, brass, and aluminum. It is also evident that the solute must remain dissolved during long storage, and the fluid must be sufficiently oxidation stable so that storage for years will not cause the separation of additives or the appearance of corrosive products (such as organic acids). A less obvious requirement for the solvent is that it have the highest possible equilibrium spreading pressure.

C. Importance of the Equilibrium Spreading Pressure

It has been known for years that numerous types of amphipathic⁴ polar organic compounds which are insoluble or slightly soluble in water will spread out over the clean, grease-free surface of water to form a uniform film. If the area available is sufficiently large, there will result an invisible layer one molecule thick. Such polar molecules are characterized by having one or more chemically active and water-attracting (hydrophilic) groups at one end of the molecule and a chemically inactive and water-repelling (hydrophobic) portion at the other. If present in excess of that needed to fully cover the water surface with a monomolecular film, any film-forming (or surface-active) liquid compound, will form floating drops in equilibrium with the monolayer. Under these conditions the monolayer will exert a constant spreading force, or two-dimensional equilibrium surface pressure F_o , which is characteristic of the compound at that temperature. This pressure can be measured with a Langmuir surface pressure balance or can be computed from measurements of the surface tensions S_w of the clean water, S_{oa} of the spreading oil, and S_{ow} of the interfacial tension at the oil-water interface by using the well known Harkins relation^{4,1} $F_o = S_w - (S_{oa} + S_{ow})$. When F_o is positive, the liquid will spread out over the water surface. When F_o is negative, the liquid will not spread even on clean water but will float as a lens. Under the latter conditions F_o cannot be measured with a hydrophil balance but must be computed from the three surface tension measurements.

⁴ The term "amphipathic" is a unique one coined by G. S. Hartley. In his work, "Aqueous Solutions of Paraffin Chain Salts" (Herman & Cie., Paris, 1936), Hartley defines the word as meaning "that the ion has an unsymmetrical duality of affinity, one end being water-attracting...and the other having an antipathy for water."

^{4,1} W. D. Harkins and A. Feldman, J. Am. Chem. Soc., 44, pp. 2665-85, (1922).

The majority of the values of F_0 available in the literature, prior to the work reported here, were given many years ago by Harkins and co-workers.^{5,6,7} The equilibrium spreading pressure F_0 is generally expressed as dynes of force per centimeter of the surface boundaries experiencing that force. For example, pure oleic acid dropped on clean, distilled water at 25°C exerts a pressure of approximately 30 dynes/cm. Few liquids are known with values of F_0 in excess of 50 dynes/cm. Vegetable oils and oxidized petroleum oils generally have values of less than 25 dynes/cm. In Table I are listed the equilibrium spreading pressures of a variety of polar organic liquids.

The majority of the results recorded are new and were obtained in connection with war work of this Laboratory reported elsewhere.^{8,9,10} They were obtained by the convenient and reliable method of Washburn and Keim^{11,12,13} which avoids the necessity of painstaking measurements of the surface tension S_{or} and the interfacial tension S_{ow} . The latter is very sensitive to purity and is the principal source of error in the calculation of F_0 from the Harkins relation.

In spraying the water-displacing fluid on equipment to be preserved, the drops of organic fluid will rarely fall upon dry metal but instead will fall on the surface of the adhering water layer. The higher the equilibrium spreading pressure on water, the more rapidly will the organic liquid spread over the surface of the water and the more completely will it cover the water, even in the presence of floating insoluble or oily films which may have contaminated its surface. For a water-displacing fluid to have optimum surface-covering powers it should have the highest obtainable spreading pressure on

⁵ W. D. Harkins and A. Feldman, J. Am. Chem. Soc., 44, pp. 2665-85, (1922).

⁶ W. D. Harkins, Colloid Symposium Monograph VI, pp. 17-40, The Chemical Catalog Company, New York, 1928.

⁷ W. D. Harkins, Alexander's Colloid Chemistry, Vol. V, pp. 12-102, Reinhold, 1944.

⁸ W. A. Zisman and D. L. Pickett, "Wetting and Spreading Agents for Cleaning Water Surfaces of Oil Films," NRL Report No. P-1930, September 1942.

⁹ W. A. Zisman and D. L. Pickett, "Spreading Agents for Cleaning Water Surfaces of Oil Films," NRL Report No. P-1984, January 1943.

¹⁰ D. L. Pickett and W. A. Zisman, "The Development of Improved Petroleum Larvacides for Mosquito Control," NRL Report No. P-2072, May, 1943.

¹¹ E. R. Washburn and C. P. Keim, J. Am. Chem. Soc., 62, pp. 1747-1749, (1940).

¹² C. P. Keim and E. R. Washburn, J. Am. Chem. Soc., 62, pp. 2318-2327, (1940).

¹³ L. F. Transue, E. R. Washburn, and F. H. Kahler, J. Am. Chem. Soc., 64, pp. 274-276, (1942).

TABLE I
Equilibrium Spreading Pressures, F_0 , of Various Polar Organic Materials

Substance	Boiling Point °C *	F_0 dynes/cm @ 25°C
N-Butanol	117.9	44.8
Diethylene glycol monolaurate	240 to 325 (e)	41.5
Sorbitan monooleate	-----	41.0
Mannacin monooleate	-----	38.3
Sorbitan dilaurate	-----	38.2
1-Hexanol	157.2	37.9
2-Ethyl-1-butanol	148.9	37.0
Cyclohexanol	161.5	34.5
Sorbitan triricinoleate	-----	33.6
Glyceryl α , γ diisoamyl ether	-----	33.1
Diglycol ricinoleate	-----	33.0
1-Ethyl cyclohexanol	-----	32.0
2-Ethyl-1-hexanol	183.5	30.8
Oleic acid	172 @ 1 mm (k)	30.0
Diethanolaminoethylphosphatidic acid	-----	28.9
p-Oxy-n-methoxyallylbenzene	253.5	27.6
Benzyl alcohol	205.2	27.4
Di-2-ethylbutyrate triethylene glycol	358.0	26.8
2-Ethyl-1-hexanoic acid	226.9 (b)	26.4
Di-2-ethylhexoate triethylene glycol	370.0	26.2
Tricaprylin	M.P. 4 to 6	26.0
Triamyl borate	220 to 280 (g)	25.8
Ethyl ricinoleate	193 @ 1 mm (d)	24.6
Lauryl α acetoxy propionate	-----	24.1
Ricinoleic acid (Tech)	250	23.5
Triamyl citrate	Dec. (i)	23.0
2-Chloro-4-tert amyl phenol	253-264 (i)	22.6
Dibutyl ether	142.4	21.9
Ethyl myristate	M.P. 10 to 12	20.7
Octyl phenoxy ethanol	160-210 @ 5 mm (h)	20.4
Diisobutyl ketone	168.1	20.1
Tricaproin	228 to 231 @ 15 mm (c)	20.1
Decylacetate	91 @ 1.5 mm (f)	19.8
Phenylundecylic acid	-----	19.5
Neatsfoot oil	-----	19.0
Myristic acid	250.5 @ 100 mm	18.1
Methyl laurate	-----	17.2
Triolein	-----	17.0
Dihexyl ether	226.2	16.6
Castor oil	-----	16.5
5-Nonanol	194.0	15.9
Ethylphenylstearic acid	212 to 226 (a)	15.9
Xylolstearic acid	290 @ 1.5 mm (a)	14.7
Xylolundecylic acid	----	14.4
2-Heptyl-1-nonanol	112 @ 1 mm (k)	14.1

TABLE I (Cont.)

Substance	Boiling Point °C *	F_o dynes/cm @ 25°C
Amyl stearate	230 to 270 @ 30 mm (g)	13.8
Decyl caproate	103 @ 1.5 mm (f)	12.9
Tetrahydronaphthylstearic acid	-----	12.4
Rapeseed oil	-----	10.5
Tricresylphosphate	264 @ 20 mm (d)	9.5
Amyl laurate	126 @ 1.5 mm (f)	8.9
Methylphenyl undecylate	-----	8.0

Legend

- (a) Department of Agriculture, Eastern Regional Research Laboratory (Dr. A. J. Stirton)
- (b) Carbide and Carbon Chemicals Corp., Synthetic Organic Chemicals, 12th Ed., 1945
- (c) Eastman Kodak Co., Eastman Organic Chemicals, 25th Ed., 1946
- (d) Fiske University, Department of Chemistry (Dr. St. Flmn Prady)
- (e) Glyco Products Co., Glyco Chemicals, 1946
- (f) University of Illinois, Department of Chemistry (Dr. C. S. Marvel)
- (g) The Reinhold Publishing Co., The Condensed Chemical Dictionary, 3rd Ed., 1942
- (h) Rohm and Haas Chemical Co. (Dr. Virgil Ware)
- (i) Sharples Chemical Co., Synthetic Organic Chemicals, 11th Ed., 1939
- (k) University of Wisconsin, Department of Chemistry (Prof. Homer Adkins)

* Unless otherwise stated the data was obtained from The Chemical Rubber Handbook of Chemistry and Physics, 30th Ed., 1947.

water and a minimum viscosity. A considerable advance should be possible by using as a solvent for the water-displacing fluid one of the more surface-active polar compounds of Table I rather than one of the hydrocarbons or mixtures of hydrocarbons of Table II.

D. Water Solubility vs. Preferential Wetting of Metals

Even after it has completely spread over a steel plate covered with water, the polar liquid will be unable to displace the water unless (a) it can submerge or dissolve or otherwise penetrate to some extent down into the water layer, (b) the polar molecules dissolved or dispersed in the water can reach or diffuse to the metal surface, and (c) the polar molecules reaching the metal can preferentially adsorb on the metal to form a very hydrophobic film (one having a sufficiently high contact angle for water). When such a combination of conditions occurs, the metal becomes inhibited or protected from rusting by the adsorbed film. If, due to evaporation or drainage, there is a clearing away of the water layer at one or more points on the horizontal surface, the thin layer of water breaks up to form a number of small drops or pools exhibiting the hydrophobic contact angle with the metal surface due to the presence of the adsorbed monolayer. The water drops can be removed if desired by evaporation or mechanical agitation of the metal parts; and even if that should consume much time, the presence of the hydrophobic film will have greatly decreased the possibility of rusting.

It might be thought that all the above requirements could be met by a polar liquid like hexanol or pentanol which, though adsorbable to form a hydrophobic film, would also be somewhat soluble in water. On the contrary, these are not widely useful materials, for the adsorbed films formed will in general evaporate too rapidly leaving the metal without any protective film. The most permanent and most effective thin-film rust-inhibiting compounds have low solubilities in water, high boiling points, and low rates of diffusion in solution. When a water displacing fluid is used which consists of a somewhat water-soluble polar solvent and a water insoluble polar rust inhibitor, the latter is carried into solution in the water as the fluid is sprayed upon it. If the layer of water adhering to the metal is reasonably thin, enough molecules of the inhibitor are dissolved or dispersed in the water to adsorb on the metal as a hydrophobic film. On the other hand, if the polar solvent is too soluble in water, it dissolves before it can spread over the water-covered surface. In such a case, more efficient spraying is needed to cover all portions of the surface.

E. Requirements for Optimum Properties

Previous research¹⁴ on the relation of equilibrium spreading pressure to molecular weight and structure showed that in each homologous series of

¹⁴ Cf. footnotes 7 and 9, page 4.

TABLE II
Equilibrium Spreading Pressures, F_o , and Related Properties of Various Hydrocarbons and Miscellaneous Compounds

Compound	Flash Point (Open Cup) $^{\circ}F$ *	Melting Point $^{\circ}C$ *	Boiling Point $^{\circ}C$ *	Percent solubility of compounds in water @ $20^{\circ}C$ *	F_o dynes/cm @ $25^{\circ}C$
<u>Aliphatic Compounds</u>					
n-Hexane	14	-94	69.0	0.01	3.5
n-Heptane	20	-90	98.5	0.005	1.7
n-Octane	57	-56	125.8	0.001	0.2
Isooctane	20 (b)	-107.5 (c)	99.2 (c)	i	4.6
n-Decane	111	-30	174.0	i	-3.0
n-Dodecane	165	-12	214.0	i	-6.0
n-Tetradecane	212 (d)	+ 5.5	252.5	i	-9.0
n-Hexadecane	230 (d)	+20.0	287.5	i	-11.8
<u>Aromatic Compounds</u>					
Benzene	13	+ 5.0	80.1	0.08	9.9
Methyl benzene (toluene)	42	-95	110.7	0.05	8.7
1,3-Dimethyl benzene (m-Xylene)	81	-53	139.0	i	6.9
Ethyl benzene	59 (d)	-94	136.2	0.02	6.3
n-Propyl benzene	86 (d)	-101	159.5	0.006	5.5
Isopropyl benzene (Cumene)	102	-97	152.0	i	6.9
sec-Butyl benzene	126 (d)	-83	173.0	i	4.7
tert-Butyl benzene	--	-58	168.6	i	5.6
1,3,5-Trimethyl benzene (mesitylene)	--	-73	176.0	i	5.5
p-Ethyl toluene	--	< -20	162.0	i	5.4
p-Isopropyl toluene (p-cymene)	97 (e)	-74	176.0	i	6.1
p-n-Butyl toluene	--	---	198.0	i	2.9
tert-Amyl benzene	--	---	190.0	i	3.2
1,2,4-Trimethyl benzene (pseudocumene)	--	-57	169.8	i	5.3
Isoamyl benzene	--	---	198.0	i	4.6

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TABLE II (Cont.)

Compound	Flash Point (Open Cup) °F *	Melting Point °C *	Boiling Point °C *	Percent solubility of compounds in water @ 20°C *	F _o dynes/cm ² @ 25°C
Naphthenic Compounds					
Cyclohexane	+2 (d)	+ 6	81.4	i	0.0 or less
Ethyl cyclopentane	--	--	103.0	i	"
Ethyl cyclohexane	--	--	131.8	i	"
1,3-Dimethyl cyclohexane	52 (d)	--	120.0	i	"
tert-Butyl cyclohexane	--	--	166.0	i	"
Hexahydrocymene	--	--	169.0	i	"
Dicyclohexylmethane	--	--	251.0	i	"
1,1-Diphenylethane	--	--	269.0	i	"
Commercial Hydrocarbon Solvents					
Solvesso #1	100 (a)	--	93 to 135 (a)	i	11.9
Varsol #1	100 (a)	--	155 to 195 (a)	i	9.7
Miscellaneous Compounds					
Carbon Tetrachloride	--	22	77	0.08	7.1
Specification 52-C-18 grade III (A)	100 (a)	--	--	----	---
Specification 52-C-18 grade III (F)	100 (a)	--	--	----	---

Legend

* Unless otherwise stated the data was obtained from The Chemical Rubber Handbook of Chemistry and Physics, 30th Ed., 1947

i Insoluble

a Government Specification

b Modern Plastics Encyclopedia, Vol. 2, 1947

c Phillips Petroleum Co., Phillips Hydrocarbons, 1946 Ed.

d The Texas Co., Physical Constants of Pure Hydrocarbons, 4th Ed., 1943

organic, polar, monofunctional compounds the spreading pressure at room temperature increased linearly as the chain length decreased or as the boiling point decreased. For such compounds, it is evident that the spreading pressure increases as the solubility in water increases. The problem, therefore, of choosing the most effective solvent for a water-displacing fluid involves compromise between several conflicting requirements. Although the lowest boiling polar compounds have the highest spreading pressures and evaporate most rapidly, they may be too soluble in water to spread well. They also have the lowest flash points and are therefore the most hazardous to use. On the other hand, the highest boiling compounds are too slow to evaporate and are too insoluble to displace water well.

III. DEVELOPMENT OF HIGHLY EFFECTIVE FLUIDS

A. Relation of Molecular Structure of Volatile Liquids to Equilibrium Spreading Pressure

It is obvious that a hydrocarbon solvent will give a fluid composition having a very low solubility in water. Adsorption of the inhibitor through an intervening layer of water will be practically nil. There are other difficulties in using hydrocarbons with respect to obtaining high equilibrium spreading pressures. These are evident after a study of the data of Table II. The spreading ability of the low molecular weight hydrocarbons is due to their volatility and condensability. A drop of the liquid spreads out because the vapor from the drop weakly adsorbs on water and condenses to form a liquid layer under the cohesive forces existing in the adsorbed film. Such a substance therefore spreads the more rapidly and exhibits the higher spreading pressure the lower the boiling point. In Figure 1 are plotted the spreading pressures of various aromatic and aliphatic low molecular weight hydrocarbons as functions of the boiling point at atmospheric pressure. In the case of aliphatic compounds a good linear plot also results when F_0 is plotted against the chain-length of the longest chain $N_{\max}$ in the hydrocarbon molecule (Figure 2). The pure higher boiling point hydrocarbons do not spread on water as can be seen from Table II. The spreading pressure F_0 then becomes negative. It is interesting to note that, before the value of F_0 for hexadecane was measured, it was estimated by extrapolating the straight line graph of the values for the pentanes through the octanes. The maximum equilibrium spreading pressure of hydrocarbon solvents which are liquid at atmospheric pressure and temperature is approximately 10 dynes/cm. The slightly higher value (11.9) of Solvesso #1 in Table II is due probably to a small concentration of either polar or volatile nonpolar impurities. It is concluded that if spreading pressures higher than 10 dynes/cm are desired, polar solvents must be used.

A systematic search for suitable polar solvents was made from among those commercially available. As only a few of the necessary spreading pressure data were to be had, the measurements were made in a constant temperature room using a Cenco "Hydrophil" film balance modified to use Teflon end-loops¹⁵ and a piston film of eicosyl alcohol. The distilled

¹⁵ H. W. Fox and W. A. Zisman, Rev. Sci. Instr., 19, p. 274, (1948).

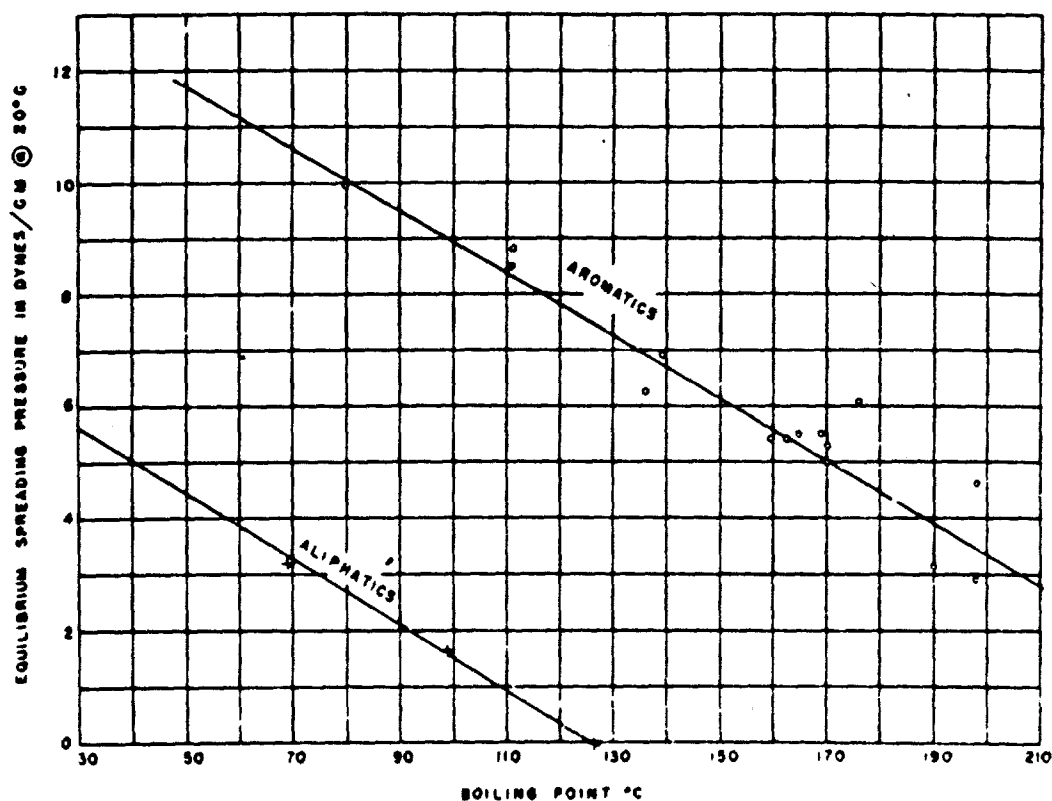


Figure 1 - Spreading Pressure of Hydrocarbons
as Function of Boiling Point

water used as substrate was maintained at $20^{\circ}\text{C} \pm 0.2^{\circ}$.

The classes of compounds studied were the alcohols, ethers, glycols, ethers, ketones, acetates, acetoacetates, lactates, carbonates, and oxalates. In all instances the compounds were the commercially available solvents which, unless otherwise noted, were used as received. Exhaustive purification was not undertaken because according to results reported in Section III C, concentrations of 5 percent or more of polar compounds did not cause a significant error in the measurement of the equilibrium spreading pressure of highly surface-active liquids. When there was any reason to believe that significant amounts of impurities were present of very much lower or higher surface activity, purification measures were employed. In Tables III, IV, and V the results are arranged by homologous series and in order of increasing molecular weight. Included also (where available) are certain physical constants of interest such as flash point, melting point, boiling point, and limits of miscibility with water.

The alcohols studied are listed in Table III. Many of these solvents are of particular interest for this investigation by virtue of ready availability.

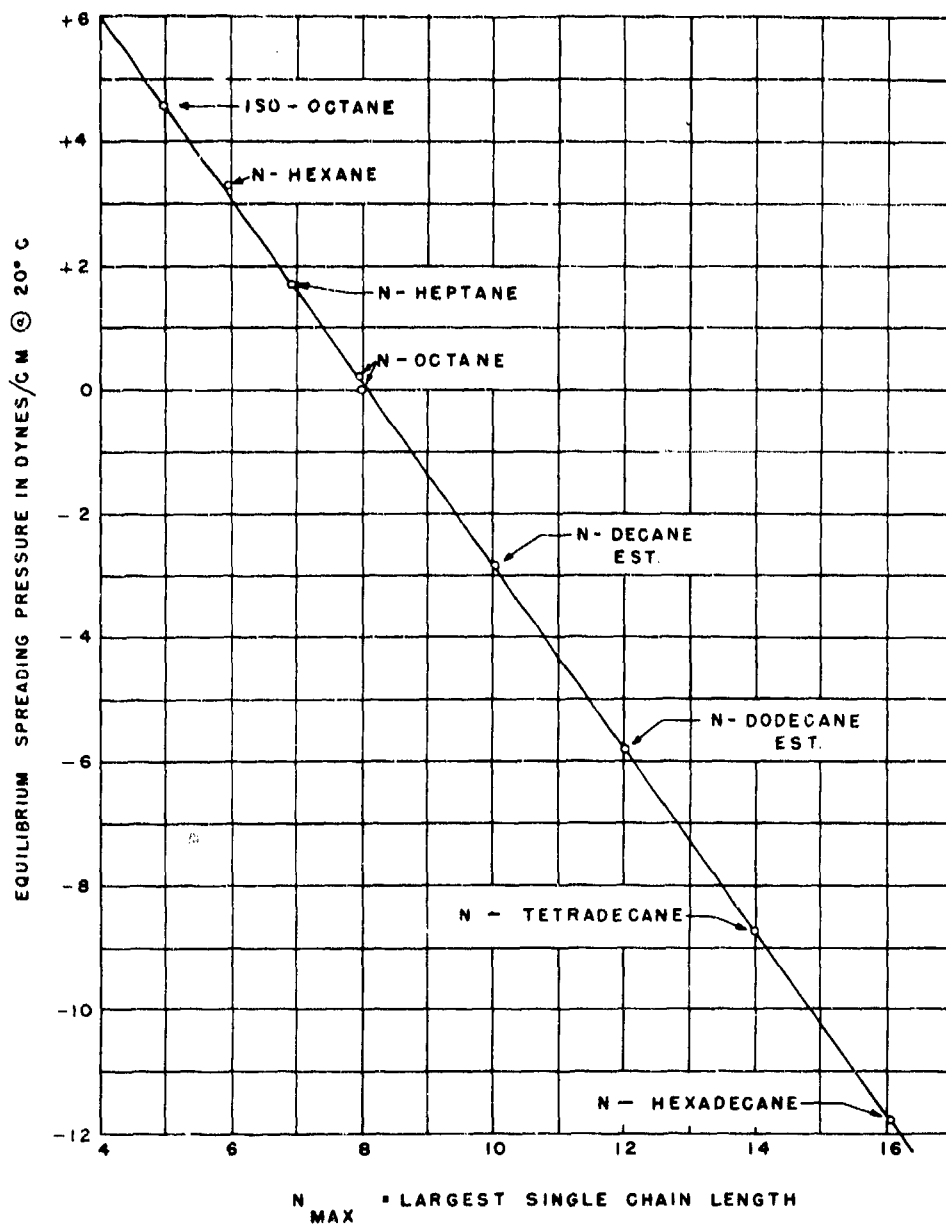


Figure 2 - Spreading Pressure of Hydrocarbons as Function of Chain Length

good stability, freedom from corrosiveness, and low rate of attack on many of the common plastic and insulating materials. It is seen that the equilibrium spreading pressure increases as the boiling point and flash point decrease. A comparison of any group of isomers shows this correlation well. Figures 3 and 4 are graphs of spreading pressure at 20°C vs. boiling point and maximum chain length respectively. In each chart a good straight line graph resulted for the unbranched alcohols when the first few members of the series were excluded, and a fair approximation to a straight line with steeper slope was obtained in Figure 3 for the branched-chain alcohols.

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TABLE III
Equilibrium Spreading Pressures, F_o , and Related Properties of Various Alcohols

Alcohol	Flash Point (Open Cup) °F *	Melting Point °C *	Boiling Point °C *	Percent solubility of water in fluid at 20°C *	Percent solubility of fluid in water at 20°C *	F_o dynes/cm at 20°C
Aliphatic						
Methanol	60	- 95.8	64.5	Complete (a)	Complete	-----
Ethanol	70	-114.4	78.3	" "	"	-----
1-Propanol	72 (b)	-127.0	97.2	" "	"	-----
2-Propanol	70	- 89.5	82.4	" "	"	-----
1-Butanol	115	- 90.0	117.3	20.1 (a)	7.7	-----
2-Butanol	75 (b)	-114.7	99.5	56.0 (a)	24.4	48.5
2-Methyl-1-propanol	81 (b)	-108.0	108.4	-----	9.5 ± 18°	<0.4
1-Pentanol	136	- 78.5	138.0	-----	2.7 ± 22°	49.3
2-Methyl-1-butanol	120 (d)	< - 70.0	128.0 (d)	-----	-----	43.3
3-Methyl-1-butanol	115 (b)	-117.2	130.5	18.0 (d)	2.67 ± 22°	44.9
2-Methyl-2-butanol	74 (b)	- 11.9	101.8	-----	12.5	47.1
3-Pentanol	100 (d)	< - 75.0	115.6 (d)	-----	-----	44.0
1-Hexanol	165	- 44.6	157.2	7.26 (a)	0.58	36.9
2-Ethyl-1-butanol	135	-----	148.9	4.56 (a)	0.43	39.1
2-Methyl-1-pentanol	129 (b)	- 90.0	132.0	-----	1.8	39.2
1-Heptanol	---	- 35.0	176.0	-----	0.1	37.3
2-Heptanol	160	-----	160.4	5.07 (a)	0.35	40.3
2,4-Dimethyl-3-pentanol	---	-----	140.0	-----	- 0.05	38.8
1-Octanol	178 (c)	- 16	195.0	-----	0.03	35.5
2-Ethyl-1-hexanol	185	- 76	183.5	2.57 (a)	0.10	35.0
1-Nonanol	---	- 5	213.0	-----	i	35.5
1-Decanol	---	- 6	231.0	-----	i	34.5
5-Ethyl-2-nonanol	235 (a)	-----	225.4	2.11 (a)	< 0.02	29.7
1-Dodecanol	---	+ 24	255.0	-----	i	solid
7-Ethyl-2-methyl-4-undecanol	285 (a)	-----	263.2	0.66	< 0.02	22.0
2-Pentyl-1-nonanol	---	-----	---	-----	-----	14.1 ± 25°C
3,9-Ethyl-6-tridecanol	310 (a)	-----	308.5	0.46 (a)	< 0.02	19.6
Cyclic						
Benzyl alcohol	205 (b)	- 15	205.2	-----	40.7 ± 17°	27.4 ± 25°C
Cyclohexanol	154	+ 22	161.5	-----	5.67 ± 15°	31.5
1-Ethyl cyclohexanol	---	-----	---	-----	-----	32.0 ± 25°C
Furfuryl alcohol	167 (b)	- 31	171	Complete	Complete	-----
Tetrahydrofurfuryl alcohol	167 (b)	< - 80	170-180	"	"	-----

(a) Carbide and Carbon Chemicals Corp., *Synthetic Organic Chemicals*, 12th Ed., 1946

(b) Modern Plastics Encyclopedia, Vol. 2, 1947

(c) The Reinhold Publishing Co., *The Condensed Chemical Dictionary*, 3rd Ed., 1942

(d) Sharples Chemicals Inc., *Synthetic Organic Chemicals*, 15th Ed., 1947

* Unless otherwise stated the data was obtained from *The Chemical Rubber Handbook of Chemistry and Physics*, 30th Ed., 1947

TABLE IV
Equilibrium Spreading Pressure, F_0 , and Related Properties of Various Ethers

Ethers	Flash Point (Open) °	Melting Point °C	Boiling Point °C	Percent solubility of water in fluid at 20°C	Percent solubility of fluid in water at 20°C	F_0 dynes/cm at 20°C
Aliphatic						
Isoronyl ether	15	-86.5	68.4	0.57 (a)	1.22	31.2
n-Butyl ether	100	-94.1	142.4	0.19 (a)	< 0.05	24.7
n-Amyl ether	146 (c)	-69.3	169.0 (c)	i (a)	i	18.1
Isoamyl ether	---	---	172.5	i (a)	i	18.7
n-Hexyl ether	170	-43 (b)	226.2	0.12 (a)	0.01	17.2
Ether Alcohols from Glycol						
Methyl cellosolve (Glycol, monomethyl ether)	115	-89.5	125.0	Complete (a)	Complete	41.2
Cellosolve (Glycol, monomethyl ether)	130	< -70	135.1	" (a)	"	40.2
Butyl cellosolve (Glycol, monobutyl ether)	165	< -100	171.2	" (a)	"	39.6
2-Ethyl butyl cellosolve (Glycol, 2-ethyl butyl ether)	180 (a)	-90 (a)	196.8 (a)	10.0 (a)	1.2 (a)	41.0
Diethyl cellosolve (Glycol, diethyl ether)	95	-74	121.4	3.4 (a)	21.0	46.7
1,4-Dioxane (Glycol, ethylene ether)	65 (a)	+11.8 (b)	101.3 (a)	Complete (a)	Complete (a)	35.7
Ether Alcohols from Diethylene Glycol						
Methyl Carbitol (Diethylene glycol, monomethyl ether)	200	-37	193.2	Complete (a)	Complete	41.6
Carbitol (Diethylene glycol, monomethyl ether)	210	< -76	201.9	" (a)	"	40.8
Butyl carbitol (Diethylene glycol, monobutyl ether)	240	-73.9	230.7	" (a)	"	40.1
Diethyl carbitol (Diethylene glycol, diethyl ether)	180	-47	187.9	" (a)	"	39.6
Terpene methyl ethers	176 (b)	---	195-225 (b)	----	0.2 (b)	28.3
Tetrahydrofuran	< 80 (e)	---	66	Complete	Complete	40.5

Legend

(a) Carbide and Carbon Chemicals Corp., Synthetic Organic Chemicals, 12th Ed., 1946

(b) Modern Plastics Encyclopedia, Vol. 2, 1947

(c) The Reinhold Publishing Co., The Condensed Chemical Dictionary, 3rd Ed., 1942

(e) E.I. Du Pont de Nemours & Co., Inc., Advertisement in Chemical & Engineering News, Vol. 25, No. 23, p. 1692.

i Insoluble

* Unless otherwise stated the data was obtained from The Chemical Rubber Handbook of Chemistry and Physics, 30th Ed., 1947

TABLE V
Equilibrium Spreading Pressure, P_0 , and Related Properties of Ketones & Esters

	Flash Point (Open Cup) °F	Melting Point °C	Boiling Point °C	Percent solubility of water in fluid at 20°C	Percent solubility of fluid in water at 20°C	P_0 dynes/cm at 25°C
Acetone	15	-95.1	56.1	Complete (a)	Complete	----
Methyl ethyl ketone	24	-86.4	79.6	----	23.4@25°C	46.2
Methyl butyl ketone	75	-56.9	127.2	----	v. sl. sol.	37.6 (f)
Ethyl propyl ketone	--	--	122.0	----	sl. sol.	33.8 (f)
Methyl n-amyl ketone	120	-26.9	130.6	1.5 (a)	0.43	35.8
Methyl hexyl ketone	---	-20.9	173.5	---	i	31.9 (f)
Diisobutyl ketone	140 (a)	-41.5 (b)	168.1 (a)	0.45 (a)	< 0.06 (a)	25.8
Acetyl acetone	105 (a)	---	140.5 (a)	4.5	16.6 (a)	31.9
Acetone alcohol (4-Hydroxy-4-methylpentanone-2)	180 (a)	---	192.2	Complete (a)	Complete	----
Methyl phenyl ketone	154 (b)	-44	169.0	---	Complete	----
Ethyl acetate	174 (b)	+19.7	202.3	----	i	21.6@25°C (g)
Butyl acetate	40	-83.5	77.1	3.3 (a)	8.72	41.9
Amyl acetate	100	-75	126.3	1.2 (a)	0.68	34.1
"Cellinsolve" Acetate (Ethylene glycol monoethyl ether acetate)	103	-78.5	142.1	0.5	0.06	31.1
	150 (b)	---	156.0	6.5	23.0	43.2
Methyl lactate	125	-66	145	Complete	Complete	----
Ethyl lactate	142 (b)	-25	154	---	"	----
Butyl lactate	178 (b)	-43	188	---	3.3	43.5
Dimethyl carbonate	151 (b)	---	89	---	15.0	40.1
Diethyl carbonate	115 (b)	-43	126	---	1.4	33.1
Diethyl oxalate	167 (b)	-42	185	---	----	29.3
Ethyl acetoacetate	185 (a)	< -80	180.7 (a)	4.9 (a)	11.6 (a)	35.2
Butyl acetoacetate	185 (a)	---	213.9 (a)	2.8 (a)	0.40 (a)	30.2
Methyl amyl acetoacetate	---	---	---	---	----	31.5

Legend

(a) Carbide and Carbon Chemicals Corp., Synthetic Organic Chemicals, 12th Ed., 1946

(b) Modern Plastics Encyclopedia, Vol. 2, 1947

(f) Harkins, W.D. and Feldman, A., (ref. 4)

(g) Transue, L.F., Washburn, E.P., and Kahler, F.H. (ref. 12)

i Insoluble

v. sl. sol. Very slightly soluble

sl. sol. Slightly soluble

* Unless otherwise stated, the data was obtained from The Chemical Rubber Handbook of Chemistry and Physics, 30th Ed., 1947

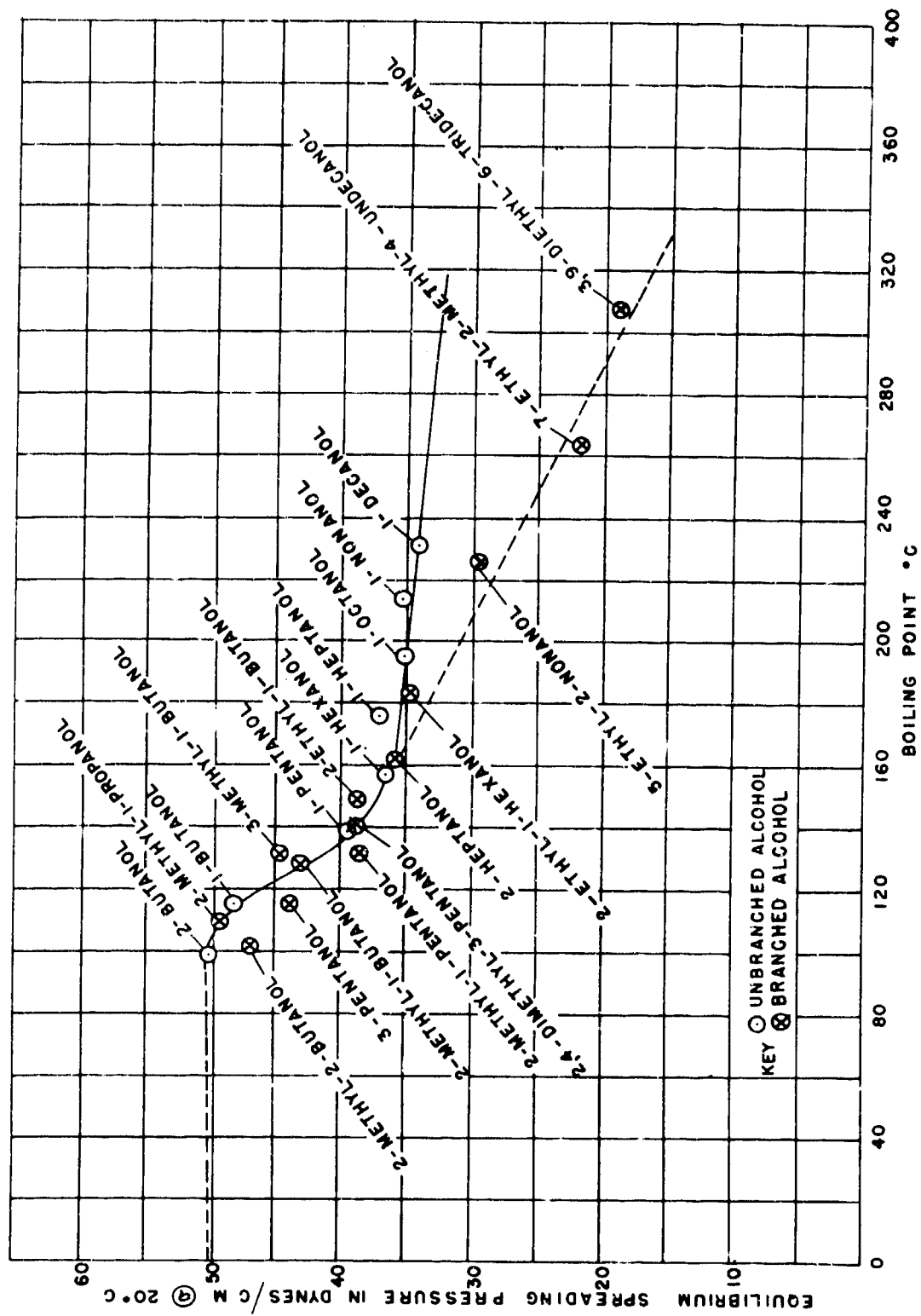


Figure 3 - Equilibrium Spreading Pressure vs. Boiling Point for Aliphatic Alcohols

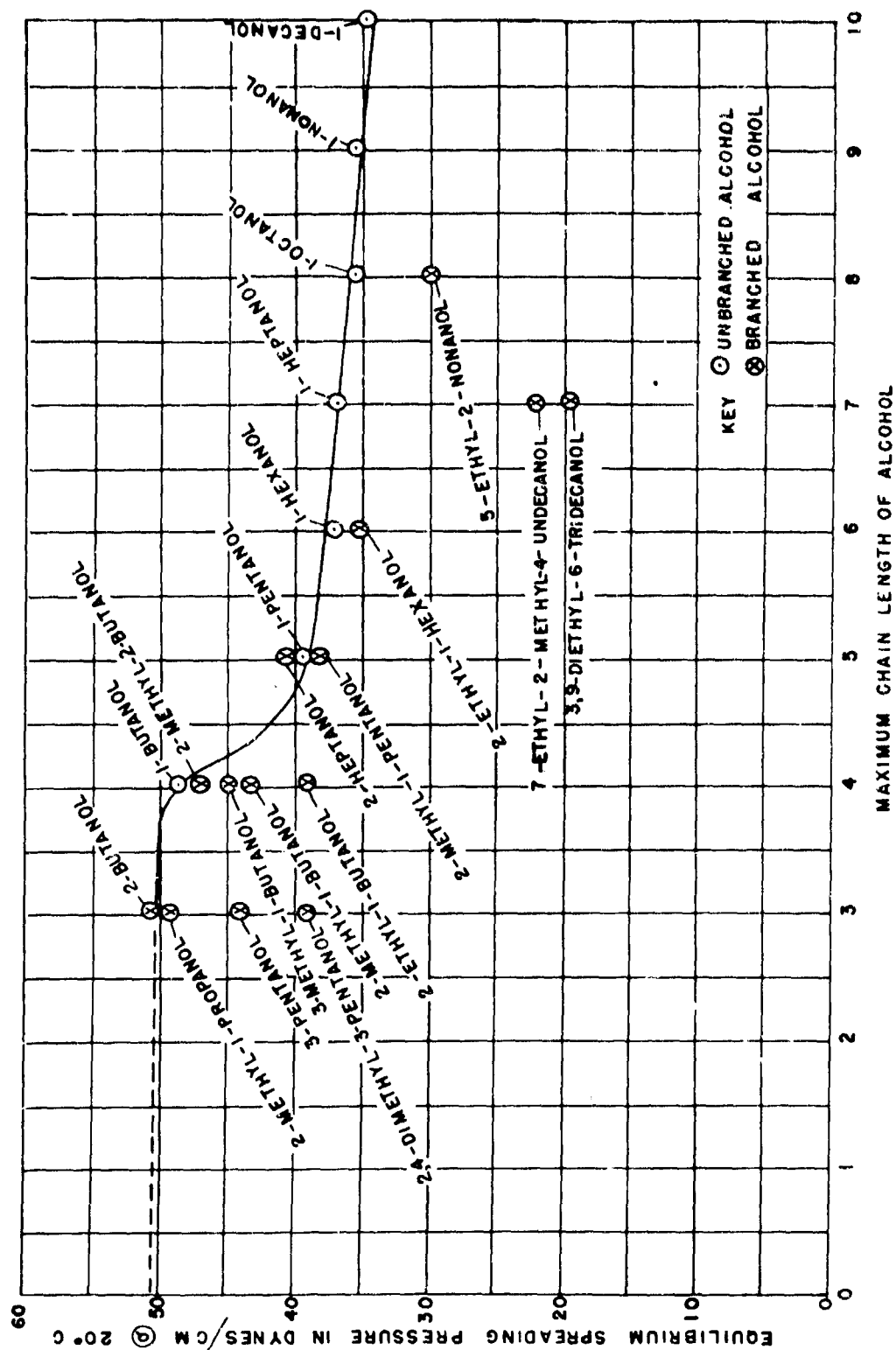


Figure 4 - Equilibrium Spreading Pressure vs. Maximum Chain Length N

The greater deviations from linearity in the series of branched alcohols in Figure 4 is not surprising since those studied are not a geometrically homologous series of compounds.

A few simple considerations show that the graphs of Figures 3 and 4 must bend over and approach a horizontal asymptote at low boiling points (or low chain lengths). It was shown earlier that:

$$F_o = S_w - (S_{oa} + S_{ow})$$

- where $S_w = 72.8$ at 20°C . In a homologous series of organic polar compounds, S_{oa} approaches a limiting value S_{lim} as the molecular weight decreases. But under these conditions S_{ow} often approaches zero, because in some series the lowest members are infinitely soluble in water. Hence F_o approaches a value F_{lim} given by

$$F_{lim} = 72.8 - S_{lim}$$

In the series of aliphatic, straight-chain, saturated alcohols of n carbon atoms, the values of S_{oa} are:

n	$S_{oa}(20^\circ\text{C})$
8	27.5
4	24.6
3	23.8
2	22.3
1	22.6

Hence, $S_{lim} = 22.5$ and $F_{lim} = 72.8 - 22.5 = 50.3$ dynes/cm, as indicated in Figures 3, 4, and 5.

For a few important branched aliphatic alcohols, S_{oa} has the following values:

Alcohol	$S_{oa}(20^\circ\text{C})$
Methyl hexyl carbinol	26.5 dynes/cm
Isoamyl alcohol	24.1 " "
Tert. butyl alcohol	20.7 " "
Isobutyl alcohol	22.8 " "
Isopropyl alcohol	21.7 " "

Hence S_{lim} depends on branched type. But S_{lim} is approximately 20 to 21. Then F_{lim} is between 51.8 and 52.8 dynes/cm, and it is close to the limit for the unbranched alcohols.

On the basis of their low flash points (under 100°F) methanol, ethanol, propanol, 2-propanol, 2-butanol, 2-methyl-1-propanol and 2-methyl-2-butanol must be considered unsatisfactory. The homologues above the hexanols are too low in volatility and probably are too insoluble in water. The most suitable alcohols are those containing 4, 5, or 6 carbon atoms per molecule. In this group the equilibrium spreading pressures range from 38 to 50 dynes/cm, the boiling points from 108 to 195°C, the flash points from 115 to 165°F, and the melting points from -108 to -40°C.

In Table IV are the data for aliphatic ethers and ether-alcohols. Here the series limit F_{lim} for the di-n-ethers is calculated to be $72.8 - 17 = 55.8$ dynes/cm @ 20°C. However, Figure 5 shows F_{lim} cannot exceed 40. It is very likely that in this series it is incorrect to assume S_{ow} approaches zero in the series limits due to the solubility in water not becoming infinite. Since for di-ethers having flash points above 100°F the equilibrium spreading pressures are all below 22 dynes/cm, they do not appear as promising as the alcohols. However, the di-ethers are twice as surface-active as the best of the hydrocarbons, and the graph of F_o vs. boiling point is also linear (Figure 5). The mono-ethers derived from ethylene glycol (the "Cellosolves") appear very promising. The equilibrium spreading pressures of methyl, ethyl, and butyl cellosolves are all over 40 dynes/cm. However, the rate of evaporation of butyl cellosolve is low, and the same is true of 2-ethyl butyl cellosolve. Diethyl cellosolve, with a value of F_o of 46.7 dynes/cm, a high evaporation rate, and a solubility in water of 4 percent is very promising even though its flash point is only 95°F. Although several ethers derived from diethylene glycol (the "Carbitols") have spreading pressures of 40 dynes/cm or more, they are not promising materials for this application because of their low rates of evaporation.

Similar data are given in Table V and Figure 5 for various aliphatic solvents including the simple ketones, acetyl acetone, acetonyl acetone, acetates, acetoacetates, lactates, carbonates, and an oxalate. Though the low-boiling ketones, acetates, and acetoacetates all have equilibrium spreading pressures of 35 to 46 dynes/cm, only a few have flash points above 100°F. Hence, the only promising fluids in this group are methyl amyl ketone, acetyl acetone, amyl acetate, cellosolve acetate, ethyl acetoacetate, butyl or propyl lactate, and possibly ethyl or methyl carbonate. Due to their greater rates of attack on rubber and plastics, these solvents, with the possible exceptions of the lactates and carbonates, have more limited uses with electrical equipment than have the alcohols. It will be noted that F_o is again a linear function of the boiling point. The series limits F_{lim} were calculated as for the alcohols and were found to be 49, 49, and 42 dynes/cm at 20°C for the n-ketones, acetates, and acetoacetates respectively.

One interesting problem concerns the possibility of adulteration of the surface active liquids used for the solvent. The use of an aliphatic hydrocarbon (Stoddard-type) solvent like Varsol #1 to dilute the polar solvent and so decrease the cost is an obvious possibility. The equilibrium spreading pressures at 20°C were measured for mixtures of butanol with 10, 20, 30, 40,

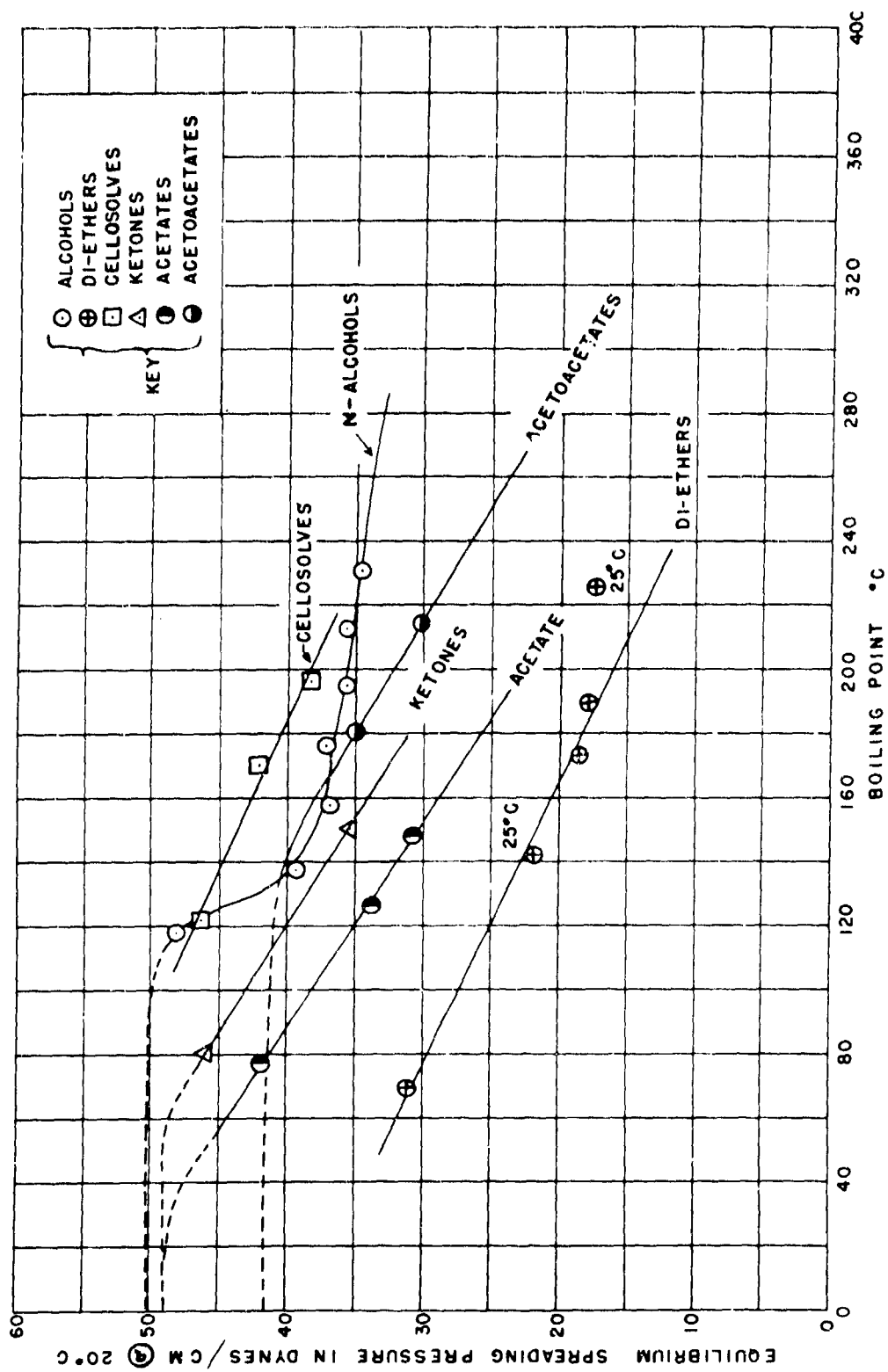


Figure 5 - Equilibrium Spreading Pressure vs. Boiling Point for Various Aliphatic Solvents

and 50 percent by volume of one of the hydrocarbon diluents, Varsol #1, cumene, or isooctane. A small, nearly linear decrease with dilution was found in the equilibrium spreading pressures up to concentrations of 50 percent. For example, dilution with 20 percent of any one of the three hydrocarbons decreased the pressure by only 2.5 dynes/cm. In short, hydrocarbon dilutions of up to 50 percent have a relatively unimportant effect on the equilibrium spreading pressure. Similar dilutions by a liquid more polar than a hydrocarbon would obviously cause an even smaller effect. The use of such diluents will, however, be limited to those with adequate volatility and desirable flash point. And there is the further and more severe limitation imposed on nonpolar diluents by the requirements of the water-displacing property.

B. Preferential Wetting and Water-Displacing Ability

An experimental procedure was required to observe the ability of a drop of organic liquid to displace water from steel or other metal surfaces. The technique found most valuable was based on the use of a Cenco "Hydrophil" tray from which the torsion head and mica float had been removed. The waxed tray was filled to overflowing with distilled water, and a 4x4x1/8-inch sheet of polished and degreased 18/8 stainless steel was supported horizontally on several glass discs so chosen that the upper surface of the steel plate could be within either one or two millimeters of the free surface of the water. The usual waxed barriers were employed to scrape the free surface clean, and a 0.025-ml drop of the organic liquid, delivered from a 0.1-ml blood pipette, was placed gently on the surface of the water. If the liquid is effective in displacing water, a hole forms in the water revealing the dry surface of the steel plate. The diameter of the hole, which increases rapidly and attains its maximum diameter within a few seconds, varies from approximately 1/2 inch to 2-3/4 inches, depending on the particular organic liquid studied. The diameter later decreases until eventually the steel surface is again completely covered by water. The time required for the complete contraction of the circular area varies with the volatility and water solubility of the organic fluid. Thus with propanol contraction was complete in five seconds while with 2-ethylbutanol several hours were required. When the organic liquid is impure, however, the contraction of the disc is not always complete. Results attained in this way are given in Table VI.

One of the least water-soluble of the organic liquids (tetradecanol) did not cause a water displacement of either the one- or two-millimeter layers. The most soluble liquids (like methanol) caused some displacement of the one-millimeter water layer but none of the two-millimeter layer. As the solubility in water increased in each homologous series, the water-displacing ability increased for both the one- and the two-millimeter layers. The maximum water-displacing ability for a homologous series was more sharply defined for the displacing of the two-millimeter than of the one-millimeter water layer. If the organic liquid test drop were made much larger or were dropped from a much greater height than that indicated, the maximum diameter of spreading and the displaceable thickness of the water layer were increased. As the liquids with the highest equilibrium spreading pressures are also the most

TABLE VI
Water-Displacing Ability and Related Properties of Various Organic Fluids *

Fluid	Specific Gravity 20/20°C	Solubility of Water in fluid % by wt. at 20°C	F ₀ dynes/cm at 20°C	Maximum diameter of area of displaced water 0.025 ml. fluid laid gently on surface of water	
				One mm. thick layer	Two mm. thick layer
<u>Alcohols</u>					
Methanol	0.7924(a)	Complete	---	0.75	Does not penetrate
Ethanol	0.7905(a)	"	---	0.75	"
1-Propanol	0.8044(a)	"	---	1.00	"
2-Propanol	0.7854(a)	"	---	1.00	"
1-Butanol	0.8109(a)	20.1(a)	48.5	2.00	1.50 recovers immediately
2-Butanol	0.8087(a)	56.0	50.4	1.75	1.50
2-Methyl-1-propanol	0.8169	---	49.3	1.75	"
1-Pentanol	0.82 (d)	---	39.5	1.75	"
2-Methyl-1-butanol	0.816(d)	---	40.1	1.75	"
3-Methyl-1-butanol	0.81 (d)	---	41.6	1.75	"
2-Methyl-2-butanol	0.81 (d)	18 (d)	43.6	2.50	0.50
3-Pentanol	0.815	---	40.8	2.00	2.00 in 15 secs.
1-Hexanol	0.8208 (a)	7.26 (a)	36.9	1.75	1.00 immediately
2-Ethyl-1-butanol	0.8328 (a)	4.56 (a)	39.1	2.00	Does not penetrate
2-Methyl-1-pentanol	0.831	5.8	36.2	1.75	"
1-Heptanol	0.8219	---	37.3	1.50	"
2-Heptanol	0.8187 (a)	5.07 (a)	36.3	1.50	"
2,4-Dimethyl-3-pentanol	0.829	---	38.8	1.75	"
1-Octanol	0.8245	---	35.5	1.60	"
2-Ethyl-1-hexanol	0.8304 (a)	2.57 (a)	35.0	2.00	"
1-Nonanol	0.8274	---	35.5	0.75	"
2-Methyl-7-ethyl-1,4-undecanol	0.8363 (a)	2.11 (a)	22.0	0.50	"
2-Heptyl-1-nonanol	0.8355 (a)	0.66 (a)	14.1@25°C	Floats	"
3,9-Diethyl-6-tridecanol	0.8475 (a)	0.46 (a)	19.6	Floats	"
Benzyl alcohol	1.0501(v)	---	27.4@25°C	1.25	1.00 recovers immediately
Cyclohexanol	0.9449(a)	---	35.1	0.75	0.50 in 30 secs.
Furfuryl alcohol	1.134	---	Sinks	2.50	0.50 immediately
Tetrahydrofurfuryl alcohol	1.109(a)	---	"	1.25	"
<u>Ether Alcohols from Glycol</u>					
Methyl cellosolve (Glycol monomethyl ether)	0.9663 (a)	Complete	41.2	1.00	Does not penetrate
Cellosolve (Glycol monoethyl ether)	0.9311 (a)	"	40.2	1.25	"
Butyl cellosolve (Glycol monobutyl ether)	0.9019 (a)	"	39.6	1.75	0.75 recovers immediately
2-Ethyl butyl cellosolve (Glycol 2-ethyl butyl ether)	0.8954	10.0	41.0	1.50	Almost penetrates
Diethyl cellosolve (Glycol diethyl ether)	0.8424	3.4	46.7	1.25	0.50 recovers immediately
<u>Ether Alcohols from Diethylene Glycol</u>					
Methyl carbitol (Diethylene glycol monomethyl ether)	1.0211 (a)	Complete	41.6	1.00	Does not penetrate
Carbitol (Diethylene glycol monoethyl ether)	0.9898 (a)	"	40.8	1.25	"
Butyl carbitol (Diethylene glycol monobutyl ether)	0.9536 (a)	"	40.1	1.25	"

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TABLE VI (Cont.)

Fluid	Specific Gravity 20/20°C	Solubility of Water in fluid % by wt. at 20°C	F ₀ dynes/cm at 20° C	Maximum diameter of area of displaced water 0.025 ml. fluid laid gently on surface of water	
				One mm. thick layer	Two mm. thick layer
<u>Ketones</u>					
Acetone	0.7911 (a)	Complete	----	1.50	Does not penetrate
Methyl ethyl ketone	0.8052 (a)	----	46.2	1.00	----
Acetyl acetone	0.975	4.5	31.9	0.50	----
Acetyl acetone	0.972	Complete	Dissolves	1.00	0.25 recovers immediately
Methyl n-nonyl ketone	0.8156 (a)	1.5	35.8	2.75	0.50
Diisobutyl ketone	0.8089 (a)	0.15	26.8	2.50	Does not penetrate
Diacetone alcohol (4-hydroxy-4-methyl pentanone-2)	0.941	Complete	Dissolves	1.25	0.50 recovers immediately
<u>Esters</u>					
Methyl lactate	1.092	Complete	Sinks	1.50	0.25 recovers immediately
Ethyl "	1.031	----	"	2.00	0.50
Butyl "	0.979	----	43.5	2.50	0.50
Diethyl carbonate	1.069	----	40.1	1.25	Does not penetrate
Diethyl "	0.975	----	33.1	2.50	----
Diethyl oxalate	1.077	----	29.3	2.25	----
Cellulosolve acetate (Ethylene glycol monoethyl ether acetate)	0.975	6.5	43.2	1.25	0.50
<u>Miscellaneous</u>					
n-Octane	0.7036	1	0.2	Does not penetrate	Does not penetrate
n-Dodecane	0.7762 (a)	1	-6.0	----	----
Benzene	0.8794	1	9.9	----	----
Toluene	0.8662 (a)	1	8.7	----	----
Varsol #1 (Boiling range 155-195°C)	----	1	9.7	----	----
Solvesso #1 (" 93-135°C)	0.821	1	11.9	----	----
Solvesso #2 (" 135-175°C)	0.858	1	10.5	----	----
Furfural	1.160	----	sinks	2.00	----
Tetrahydrofuran	0.854	----	40.5	1.50	0.25
Terrene methyl ethers (h)	0.912	----	28.3	0.50	Does not penetrate
Pentamethylene glycol (e)	0.994	----	Dissolves	0.75	----
Ethylhexylene glycol (a)	0.942	11.7	41.9	1.25	----

*Key Same as Tables III, IV and V.
(h) Hercules Powder Company

water-soluble, it is evident that there must be a compromise between obtaining the optimum spreading ability upon water and the optimum ability to displace water from metals.

These results are in complete agreement with the simple theory already advanced in Section II-D. The most water-soluble liquids are the least able to adsorb from a dilute solution to form a hydrophobic film on the metal sheet. The larger the drop of organic liquid, the more concentrated the water solution in the vicinity of the impact area. Hence, the larger the test drop, the more effective the fluid in displacing thick layers of water. Obviously, increasing the specific gravity of the test drop will increase the ability to penetrate and displace thick layers of water. The effectiveness in displacing water would be increased by using a liquid with even greater affinity for the metal than those studied here. However, there is danger of corrosion, since the most adsorbable compounds (such as acids) are the most reactive.

On considering the need for both high spreading pressure and high water-displacing ability, it is concluded that of the aliphatic alcohols studied the best water-displacing fluids are those having from four to six carbon atoms per molecule. The best of the cyclic alcohols is furfuryl alcohol. The best of the available ether-alcohols and ethers is butyl cellosolve, the second choice being diethyl cellosolve. Of the ketones methyl amyl ketone is best, and a second choice is diisobutyl ketone. The most satisfactory of all the esters are butyl and propyl (or even ethyl) lactates, diethyl carbonate, and "cellosolve" acetate.

The advantages have already been discussed of diluting the solvent of the water-displacing fluid with a cheaper nonpolar fluid, such as a volatile hydrocarbon. Mixtures of 1-butanol with the aliphatic Stoddard solvent, Varsol #1, were used in the water-displacing experiment on a one-millimeter layer of water on steel. As usual a test drop of the organic fluid of 0.025 ml was used. In Figure 6 the ordinate is the maximum diameter attained by the hole in the water layer. The abscissa is the volume percent of Varsol #1 in butanol. As can be seen, even a 5 percent dilution of the butanol is sufficient to decrease the diameter of displacement from 3 inches to 2¼ inches, while a 10 percent dilution decreases the area nearly in proportion to the degree of dilution. Use of from 20 to 80 percent of Varsol was equally effective in displacing the one-ml layer of water, but the water-displacing property disappeared rapidly when dilutions of over 80 percent were used. The results were not greatly improved when the test drop was released one inch above the water level.

Sensitivity to dilution limits the use of hydrocarbon or other water-insoluble diluents. It is concluded that a few percent of volatile hydrocarbons can be tolerated, but higher concentrations will considerably decrease the water-displacing property of the fluid. It is possible, however, that proportions of hydrocarbons or low-polarity volatile liquids up to 15 percent by volume may be used advantageously as mutual solvents or coupling agents for the rust-inhibiting solute. Some loss in water-displacing ability can be compensated by the use of more-water-displacing fluid in practical application.

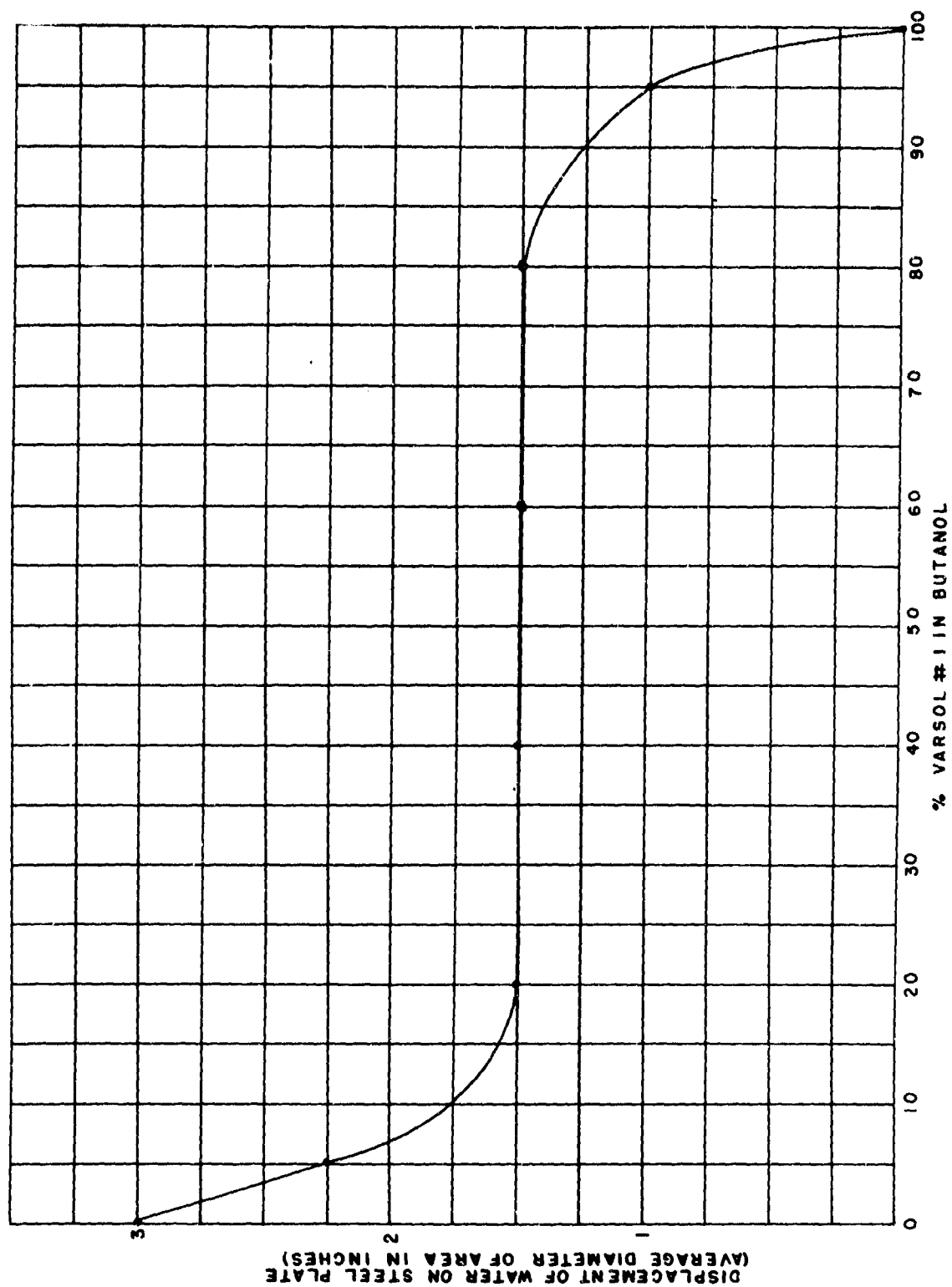


Figure 6 - Displacement of Water Layer 1 mm. Thick from Steel Plate
Test Drop = 0.025 ml

C. Polar Compounds for Rust-Inhibiting Solutes

There are numerous good rust-inhibiting compounds suitable for addition to the water-displacing fluids. The classes of particular promise for this investigation are:

- (a) Monocarboxylic acids, such as the long-chain saturated or unsaturated acids, the aryl alkyl branched acids, and the naphthenic acids;
- (b) Salts of carboxylic acids, such as the alkali, the alkaline earth, or the polyvalent salts of the acid in group (a);
- (c) Salts of sulfonic acids, such as the aliphatic, the aromatic, the alkyl aryl sulfonates or the petroleum sulfonates;
- (d) Salts of phosphoric acid derivatives, such as salts of the mono- and di-esters of phosphoric acid;
- (e) Esters of carboxylic, sulfonic, or phosphoric acids of groups (a), (c), and (d) derived from alcohols of one to six hydroxyls;
- (f) Ammonium compounds of the organic acids of groups (a), (c), and (d) reacted with an aliphatic, cyclic, or aromatic amine;
- (g) Amine nitrates, such as the diisopropyl, diisobutyl, and dicyclohexyl derivatives.

The characteristics of these compounds as rust inhibitors have been discussed in earlier reports of this Laboratory.^{17,18,19,20} Their addition to the highly surface-active solvents such as butanol, in proportions up to several percent, alters only slightly the equilibrium spreading pressure of the solvent. This is not surprising since such solutes and solvents both have high spreading pressures of about the same magnitude. The resulting solutions were used for the comparative experiments on water-displacing and rust-inhibiting properties which are described in Section III-E.

Because of their great corrosiveness after long contact, the inhibitors of class (a) are not suitable for use where nonferrous metals like copper, brass, lead, solder, and bearing materials are present. Most satisfactory of the inhibitors of classes (b) and (c) are the polyvalent salts of the long-chain acids or other high-molecular-weight amphipathic acids. The principal difficulty encountered with such compounds is their low solubility in many of the most suitable solvents for the water-displacing fluid composition. Few suitable compounds of class (d) are commercially available, and only those having good hydrolytic stabilities are useful since a mono-basic phosphoric acid is more corrosive to the common metals than are the

¹⁷ Cf. footnotes 1, 2, and 3, p. 2.

¹⁸ L. W. Beck, F. S. Cluthe, and J. K. Wolfe, "The Preparation of Metallic Arylstearates," NRL Report No. P-2787, January 1946

¹⁹ K. L. Temple and J. K. Wolfe, "Chemical Investigation of Amine Nitrate Vapor-Phase Inhibitors," NRL Report No. P-2578, July 1945

²⁰ H. R. Baker, "Properties, Naval Uses and Effect on Non-Ferrous Metals of Shell Vapor-Phase Inhibitors VPI 220 and 260," NRL Report No. P-3047, January 1947

carboxylic acids. Many of the inhibitors in class (e), however, are very satisfactory because they are cheap and are sufficiently soluble in the solvents used. The best of those found to date are the fatty acid partial esters of either a glycol, a glycerol, a sorbitol, a mannitol, or an anhydro sorbitol or mannitol. The acids particularly useful in preparing such esters are the saturated, the unsaturated, or the hydroxy acids containing from 12 to 20 carbon atoms per molecule. Many valuable inhibitors are found in class (f). These are hydrogen-bonded compounds formed by the reaction of any of the low- (or high-) molecular-weight amphipathic amines which may be aliphatic, naphthenic, or aromatic, with any high- (or low-) molecular-weight amphipathic carboxylic or sulphonic acid. The only commercially available amine nitrite inhibitors of class (g) are those derived from diisopropyl, diisobutyl, or dicyclohexyl amine. These are given in the order of decreasing volatility. All the nitrites are effective rust inhibitors for ferrous metals, but they attack certain nonferrous metals. The effect on the common nonferrous metal has been fully described in earlier work of this Laboratory.²¹ These inhibitors will eventually volatilize, and the inhibition of the surface to corrosion will disappear. Nevertheless, for some applications such a temporary inhibition may be preferable. Experiments are in progress on the duration of corrosion inhibition of steel by a water-displacing fluid containing an amine nitrate.

For these reasons, the most promising solvents, considering flash point or melting point, evaporation rate, equilibrium spreading pressure, and water-displacing ability, are:

- (a) Aliphatic straight chain alcohols, containing 4, 5, or 6 carbon atoms and having flash points over 100°F, such as 1-butanol, 1-pentanol, 3-methyl-1-butanol, 2-methyl-1-butanol, 3-pentanol, and 2-ethyl-1-butanol;
- (b) Cyclic alcohols such as furfuryl alcohol or tetrahydrofurfuryl alcohol;
- (c) Butyl cellosolve or diethyl cellosolve;
- (d) Methyl amyl or diisobutyl ketone, or acetyl acetone;
- (e) Amyl acetate, "cellosolve" acetate, or ethyl acetoacetate;
- (f) Butyl, propyl, or ethyl lactate;
- (g) Diethyl carbonate.

D. Considerations of Effects on Plastics

The more volatile the solvent, the less will be the effect on plastics and insulation. But for the same volatility, there will be a difference in the rate of attack depending on the polar group. The aliphatic alcohols appear to be the best group, with furfuryl alcohol, tetrahydrofurfuryl alcohol, the cellosolves, the acetates, lactates, ketones, and diacetone alcohol, and the carbonates following in order of decreasing usefulness. Considering odor, the pentanols and hexanols are preferable to the butanols. To save

²¹ Cf. footnote 19 on p. 26.

cost, mixed C₄, C₅, and/or C₆ aliphatic alcohols will serve if the flash points are over 100°F and if no high-boiling materials are used. The latter, of course, greatly increase the evaporation time of the solvent.

The more volatile of the organic liquids should not be harmful when rapid evaporation of the water-displacing fluid can take place. An occasional application causing concern is that where contact with plastics is prolonged either by entrapment of the liquid or through poor circulation of air.

E. Storage of Fluids and Antioxidants

During storage of water-displacing fluids it is possible for serious deterioration to take place. Storage for six months or more may cause precipitation of rust inhibitors, such a result being common when soaps, naphthenates, and sulfonates are used. Storage test are desirable since military needs often demand long shipments and extended storage times, sometimes under adverse conditions. The atmospheric oxidation of the solvent or solute during storage may cause the formation of undesired acids, gums, and precipitates. As in the storage of gasolines and oils, the rate of oxidation accelerates rapidly with increasing temperature so that tropical storage is a serious problem. Where the corrosion inhibitor is a soap containing any of the more active oxidation-accelerating metals, the storage life may be much too short.

Accordingly, the oxidation stabilities of some of the new water-displacing fluid compositions were examined using the standard gasoline oxidation pressure bomb test (ASTM D525-46). The usual 50-ml sample was stored at 100 psi and 10 °C and the length of the induction period was observed on a pressure recorder. Tests were also made with the prior addition to each fluid of 0.1 percent by weight of one of the several well known gasoline antioxidants.²² The results are given in Table VII.

The fact that 1-butanol has an induction period of eight hours is indicative of fair storage stability. Contact with soap rust inhibitors or with catalytic metals like lead, copper, or iron will shorten the induction period. If experience with the storage stability of gasoline is indicative, however, the one-year storage problem will not be severe. No detrimental effect resulted from dilution with aliphatic hydrocarbon solvents; instead, the induction period was increased to 30 hours. The addition of cumene somewhat decreases the induction period. The response to the addition of any of the well known gasoline antioxidants was excellent, and it is evident that the addition of 0.1 percent by weight either of PX441, 24M6B, UOP4 or UOP5 is sufficient for storage purposes. This holds true even with the addition to the fluid composition of 1 percent by weight of any of the classes of polar-type rust inhibitors described in Section III-C. Of the polar inhibitors, the amine nitrite had the greatest effect in depressing the induction period.

²² C. D. Lowry, Jr., Oil and Gas J. 46, pp. 211-215, (1948)

TABLE VII
Summary of Oxidation Tests on Water-Displacing Fluids
(Using Pressure Bomb Test ASTM D525-46)
(Temp. 100°C, Initial Pressure 100 ± 2 psi)

Test No.	Composition of Water-Displacing Fluid	Induction Period (hrs)
1	1-Butanol	8
2	1-Butanol + 0.1% PX441	>48
3	1-Butanol + 0.1% 24M6B	>216
4	50% 1-Butanol + 50% Varsol	30
5	50% " + 49.9% " + 0.1% PX441	>48
6	50% " + 50% cumene	7½
7	50% " + 49.9% " + 0.1% PX441	13½
8	50% " + 25% Varsol + 24.9% cumene + 0.1% 24M6B	10
9	50% " + 25% Varsol + 24.9% cumene + 0.1% PX441	11
10	98.9% 1-Butanol + 1% glyceryl mono & di oleate + 0.1% PX441	>216
11	98.9% " + 1% dicyclohexyl ammonium nitrite + 0.1% PX441	31
12	98.9% " + 1% dodecyl ammonium laurate + 0.1% PX441	>72
13	98.9% " + 1% sorbitan monooleate + 0.1% UOP4	>72
14	98.9% 2-Ethyl-1-butanol + 1% glyceryl mono & di oleate + 0.1% UOP5	>72
15	50% 1-Butanol + 25% Varsol + 23.9% cumene + 1% glyceryl mono and di oleate + 0.1% 24M6B	22
16	50% 1-Butanol + 25% Varsol + 23.9% cumene + 1% glyceryl mono and di oleate + 0.1% PX441	20
17	78.9% 1-Butanol + 20% Varsol + 1% active ingredient of barium naphthenate + 0.1% PX441	>72
18	77.9% 1-Butanol + 20% Varsol + 1% active ingredient of barium petroleum sulfonate + 0.1% PX441	>72

Key to Antioxidants:

PX441 = 2,6-Ditertiarybutyl, 4-methylphenol

24M6B = 2,4-Dimethyl, 6-tertiary butylphenol

UOP4 = N-Butylaminophenol + small amount of butylphenylenediamine

UOP5 = Di-sec-butyl-p-phenylenediamine

This is no doubt due to the instability of such compounds at temperatures as high as 100°C, and the oxidation bomb test may have been too severe.

It is believed that an induction period of 24 hours is ample for any expected storage conditions. Hence, usually not over 0.1 percent of one of these antioxidants is needed. Except when 1 percent of an amine nitrite, or when much over 1 percent of a rust inhibitor, is used, from 0.02 to 0.05 percent of the antioxidant will suffice. Such low antioxidant concentrations are economical and should not make the water-displacing fluid corrosive to the common metals. Long-term storage and corrosion tests have been started.

F. Some Promising Compositions

The most promising solvents found to date for use in preparing highly effective water-displacing fluids are in order of preference: 1-butanol, 1-pentanol, 3-methyl-1-butanol, 2-methyl-1-butanol, 2-ethyl butanol, butyl cellosolve, methyl amyl ketone, butyl lactate, and diethyl carbonate. Any one of these diluted with up to 20 percent of Varsol #1 or equivalent Stoddard solvent will be less effective in water-displacing ability but will still be better than present commercially available fluids. The rust-inhibiting solutes are glyceryl oleates, sorbitan oleates, salts of high-molecular-weight naphthenic acids, salts of high-molecular-weight petroleum sulphonic acids, high-molecular-weight ammonium compounds like dodecyl ammonium laurate, and ammonium nitrites such as dicyclohexyl-, diisopropyl-, and diisobutyl ammonium nitrite. The nitrites are recommended where it is desired to have left no residual film some days after drying and standing. The concentration of polar rust inhibitor recommended for general use is 1 percent. Higher concentrations are desirable only where long-term or outdoor storage will follow use of the water-displacing fluid. Any one of the four antioxidants described in the preceding section (see Table VII) will behave satisfactorily, and a concentration of from 0.025 to 0.10 percent will suffice for most uses.

Of the compositions shown in Table VIII, certain ones are recommended for immediate testing and use as water-displacing fluids. Fluids 1, 2, 3, and 7 are recommended for tests on electrical equipment. Fluids 8, 9 and 10 are recommended if a higher flash point is important enough to justify slower evaporation rates.

IV. LABORATORY EVALUATION OF WATER-DISPLACING FLUIDS

A. Effectiveness of One-Drop Test

A simple experiment was devised to observe the comparative water-displacing characteristics of the organic fluids using thin layers of water on horizontal surfaces of cold-rolled steel. Specimens 3-cm square were cut from 1/32-inch SAE 1020 steel sheet, carefully polished with 5/0 sandpaper, and then degreased by one or more boiling treatments in cp benzene followed by one in cp ethyl ether. So prepared, the metal surfaces remained uniformly wet when dipped into and removed from distilled water.

The wet panels were placed in a horizontal position. Then, using a 5-ml hypodermic syringe, fitted with a No. 25 stainless steel needle, a 0.02-ml

TABLE VIII

Fluid No.	Solvent	Diluent	Rust Inhibitor	Antioxidant and Concentration
1	1-Butanol	None	1% glyceryl mono- and di-oleate	PX441; 0.025%
2	1-Butanol	15% Varsol # 1	" " "	" "
3	1-Butanol	30% Varsol # 1	" " "	" "
4	1-Butanol	15% Varsol # 1	1% naphthenate Zn Barium or Strontium	" 0.05%
5	" "	15% Varsol # 1	1% Ca or Ba petroleum sulfonates	" 0.05%
6	" "	15% Varsol # 1	1% Dodecylammonium laurate or dicyclohexyl ammonium laurate	" "
7	" "	None	Dicyclohexyl ammonium nitrite	" 0.10%
8	2-Ethyl-1-Butanol	None	Glyceryl mono- and di-oleate	" 0.025%
9	Butyl cellosolve	None	Glyceryl mono- and di-oleate	" 0.05%
10	Furfuryl alcohol	None	" " " "	" 0.05%

Note: Varsol # 1 is a Stoddard type solvent in the boiling range 315-385°F having a minimum flash point of 100°F.

drop of the fluid was immediately allowed to fall on the center of the specimen from a height of 1 cm. After thirty seconds, the maximum diameter of the dry area was noted. In the case of 1-butanol, the spreading drop pushed back the water layer to form a dry circular area 3 cm in diameter.

After the drop of solvent had evaporated, the dry area contracted until the entire area was again wetted by water. If the solvent contained a small proportion of a higher boiling organic impurity, the dry area contracted more or less completely depending on the nature and amount of the impurity. If the solvent contained one of the polar rust inhibitors of high molecular weight, the dry area did not contract at all. This is a simple, sensitive, one-drop test for freedom from high boiling or polar hydrophobic film-forming impurities.

Plotted in Figure 7 is the maximum diameter of the area of water displaced on wet steel vs. the equilibrium spreading pressure on water for many of the solvents studied in this investigation. Due to inadequate control of the test drop size, much scattering of the graphical points is evident, but

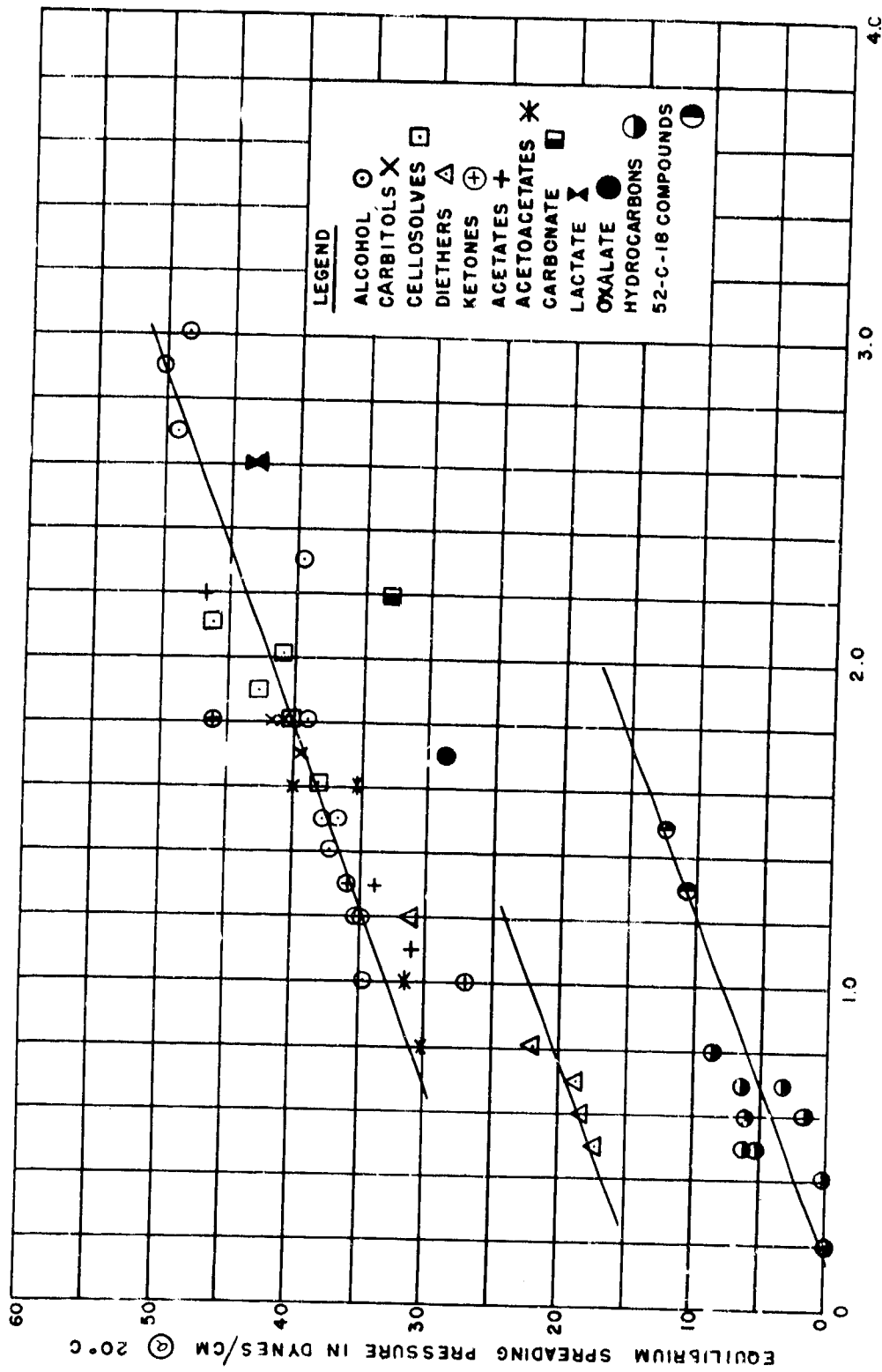


Figure 7 - Relation Between Equilibrium Spreading Pressure and Diameter of Circular Area Cleared by One Drop of Test Fluid

obviously the points cluster about the indicated straight line. From this it is seen that the fluids studied can be separated into two classes. One class of fluids exhibits relatively high spreading pressures on water (20 dynes/cm or more) and also is the most effective in displacing water films from steel surfaces. This class included many hydrophilic types such as the alcohols, cellosolves, ketones, carbitols, acetates, acetoacetates, and ethers. The other class exhibits low spreading pressures on water (10 dynes/cm or less) and is the least effective in water-displacement from steel. This class includes aliphatic or aromatic hydrocarbons, petroleum solvents, and the 52-C-18 specification fluids examined to date.

The diameter of the displaced-water area on steel from one drop of the water-displacing fluid, in which a good rust inhibitor has been dissolved, is shown in Table IX. Here again, 1-butanol containing rust-inhibiting additives exhibited the greatest spreading tendencies of any of the fluids examined. In this test, the thinness of the layer of water on the steel, and the momentum given the drop by releasing from a height of 1 cm, together emphasize the importance of the equilibrium spreading pressure and subordinate the importance of water solubility.

B. Further Tests on Rust Preventive Properties

The rust-inhibiting property of the adsorbed film, left after the evaporation of a drop of the solvent (approximately 0.02 ml), was measured by placing a drop of distilled water (approximately 0.02 ml) in the middle of the dry, film-covered area. Thereafter the steel specimen was covered with a Petri dish to retard evaporation of the water drop. Since the surface of the specimen was covered with a hydrophobic film, the water drop formed a definite contact angle at the water-film interface and did not spread or run off the specimen. Where rusting did not occur quickly, water was added to the drop each 24 hours, thus compensating for losses by evaporation. The times required for rusting to begin are shown in Table IX.

It will be noted that the time protection is afforded by the film varies with the concentration of inhibitor. The durability of the film does not increase linearly with the concentration of inhibitor, and rapidly diminishing returns set in for 1 percent or more of the inhibitor. No saturation occurs, however, so that the durability with 5 percent of the inhibitor may be approximately 50 percent greater than for 1 percent. The appropriate concentration must be determined by practical considerations such as cost, service needs, and tolerance for thick long-lasting films on equipment. Excluding the amine nitrites, no important differences are discernible among the different high-molecular-weight inhibitors of Classes A, B, C, E, and F. Considerations such as solubility in the organic base of the water-displacing fluid and cost will determine which compounds are used. The effectiveness of amine nitrites increases rapidly as concentration is increased from 0.1 percent to 0.5 percent, but a concentration of 0.5 percent or more is recommended. The optimum concentration will have to be determined by future experience and the time required for complete evaporation.

Another practical test on the rust-inhibiting properties of the residual films was carried out using the fog cabinet method developed by this

TABLE IX
Rust Inhibition of Water-Displacing Compositions

Fluid	Inhibitor	Inhibitor percent by weight	Displacing of water film on steel (diameter of water area displaced, cm.)	Time before failure, hrs.	
				Spot Test at 75-80°F	Fog Cabinet Test at 100°F
1-Butanol	without additive	0.0	3.00	between 0 and 1 hr.	1
	Naphthenic acid MW 188	0.1	2.75	" 8 " 16 hrs.	
	" "	0.5	2.50	" 16 " 24 "	
	" "	1.0	2.25	" 32 " 40 "	
	" "	5.0	2.25	" 32 " 40 "	
	" MW 247	0.1	2.75	" 16 " 24 "	
	" "	0.5	2.50	" 24 " 32 "	
	" "	1.0	2.25	" 40 " 48 "	
	" "	5.0	2.25	" 40 " 48 "	
	" MW 440	0.1	2.50	" 24 " 32 "	
	" "	0.5	2.25	" 32 " 40 "	
	" "	1.0	2.25	" 40 " 48 "	
	" "	5.0	2.00	" 40 " 48 "	
	Xylolstearic acid	0.1	2.75	" 24 " 32 "	
	" "	0.5	2.50	" 32 " 40 "	
	" "	1.0	2.50	" 40 " 48 "	
	" "	5.0	2.25	" 40 " 48 "	
	Xerylstearic acid	0.1	2.75	" 24 " 32 "	
	" "	0.5	2.75	" 32 " 40 "	
	" "	1.0	2.50	" 40 " 48 "	
	" "	5.0	2.00	" 40 " 48 "	
	Dodecylphenylstearic acid	0.1	2.75	" 8 " 16 "	
	" "	0.5	2.75	" 16 " 24 "	
	" "	1.0	2.50	" 24 " 32 "	
	" "	5.0	2.00	" 40 " 48 "	
	Zinc naphthenate	0.1	2.00	" 16 " 24 "	
	" "	0.5 *	1.50	" 32 " 40 "	
	" "	2.0 *	----	" " " "	72
	Magnesium Xylolstearate	0.1	2.25	" 16 " 24 "	
	" "	0.5 *	2.00	" 32 " 40 "	
	" "	2.0 *	----	" " " "	72
	Calcium Xylolstearate	0.1	2.25	" 16 " 24 "	

Table IX - (Cont.)

Fluid	Inhibitor	Inhibitor Percent by weight	Displacing of water film on steel (diameter of water area displaced, cm.)	Time before failure, hrs.	
				Spot test at 75-80°F	Fog Cabinet Test at 100°F
1-Butanol	Calcium Xylolstearate	0.5 *	2.00	between 32 and 40 hrs.	96
	Barium naphthenate	2.0	-----	-----	72
	Barium petroleum sulfonate	2.0	-----	-----	
	Sodium "	0.25	2.80	" 32 " 40 "	
1-Butanol	" "	0.5	2.50	" 40 " 48 "	
	Sorbitan monooleate	0.1	2.80	" 8 " 16 "	
	" "	0.5	2.60	" 16 " 24 "	
	" "	1.0	2.50	" 24 " 32 "	
	" "	2.0	-----	-----	120
	Carbitol ricinoleate	5.0 *	2.25	" 32 " 40 "	
	" "	0.1	2.50	" 8 " 16 "	
	" "	0.5	2.50	" 16 " 24 "	
	" "	1.0	2.25	" 24 " 32 "	
	" "	5.0 *	2.00	" 32 " 48 "	
	Glycerol mono- & dioleate	0.1	2.90	" 8 " 16 "	
	" "	0.5	2.75	" 16 " 24 "	
	" "	1.0	2.50	" 24 " 32 "	
	" "	2.0	-----	-----	120
	Decyl ammonium laurate	5.0 *	2.25	" 40 " 48 "	
	" "	0.1	2.75	" 8 " 16 "	
	" "	0.5	2.50	" 16 " 24 "	
	" "	1.0	2.50	" 24 " 32 "	
	" "	2.0	-----	-----	48
	" "	5.0 *	2.25	" 32 " 40 "	
	Cyclohexyl ammonium 2-ethyl caproate	2.0	-----	-----	48
	Dicyclohexyl ammonium laurate	0.1	2.75	" 8 " 16 "	
	" "	0.5	2.50	" 16 " 24 "	
	" "	1.0	2.25	" 24 " 32 "	
	" "	5.0 *	2.00	" 32 " 40 "	
	Cetyl dimethyl ammonium xylolstearate	2.0	-----	-----	72
	Diisopropyl ammonium nitrite	0.1	3.00	" 8 " 16 "	
	" "	0.5	2.90	>48	

Table IX - (Cont.)

Fluid	Inhibitor	Inhibitor percent by weight	Displacing of water film on steel (diameter of water area displaced, cm.)	Time before failure, hrs.	
				Spot Test at 75-80°F	Fog Cabinet Test at 100°F
1-Butanol	Diisobutyl ammonium nitrite	1.0	2.80	>48	
	Dicyclohexyl ammonium nitrite	0.1	3.00	between 8 and 16 hrs.	
	"	0.5	3.00	>48	
	"	1.0	2.90	>48	48
1-Pentanol	"	2.0	----	-----	1
	without additive	0.0	2.30	0 " 1 "	
	Naphthenic acid MW 188	0.5	2.10	24 " 32 "	
	Xylolstearic acid	P.S	2.10	24 " 32 "	
	Zinc naphthenate	0.1 *	2.00	32 " 40 "	
	Magnesium xylolstearate	0.1	2.00	32 " 40 "	
	Sodium petroleum sulfonate	0.25	2.00	32 " 40 "	
	Glycerol mono- & di- oleate	0.5	2.10	24 " 32 "	
	Dicyclohexyl ammonium laurate	0.5	2.00	16 " 24 "	
	Dicyclohexyl ammonium nitrite	0.5	2.20	>48	
	without additive	0.0	1.8	0 " 1 "	1
	Naphthenic acid MW 188	0.5	1.6	24 " 32 "	
	Xylolstearic acid	0.5	1.6	24 " 32 "	
	Zinc naphthenate	0.1	1.3	32 " 40 "	
Methyl cellosolve (Diethylene glycol monomethyl ether)	Magnesium xylolstearate	0.1 *	1.2	32 " 40 "	
	Sodium petroleum sulfonate	0.25 *	1.3	32 " 40 "	
	Glycerol mono- & dioleate	0.5 *	1.5	32 " 40 "	
	Dicyclohexyl ammonium laurate	0.5	1.5	24 " 32 "	
	Dicyclohexyl ammonium nitrite	0.5	1.5	>48	
	without additive	0.0	2.0	0 " 1 "	1
	Naphthenic acid MW 188	0.5	1.8	24 " 32 "	
	Xylolstearic acid	0.5	1.8	24 " 32 "	
	Zinc naphthenate	0.1 *	1.6	32 " 40 "	
	Magnesium xylolstearate	0.1	1.6	32 " 40 "	
	Sodium petroleum sulfonate	0.25 *	1.6	32 " 40 "	
	Glycerol mono- & dioleate	0.5 *	1.7	32 " 40 "	
	Dicyclohexyl ammonium laurate	0.5	1.6	24 " 32 "	
	Dicyclohexyl ammonium nitrite	0.5	1.8	>48	96
52-C-18, grade III, sample 1			1.5	40 " 48 "	
			1.3	32 " 40 "	72

Legend

* solution becomes cloudy on storage

RESTRICTED

Laboratory.^{22,23} Polished SAE 1020 steel specimens $1\frac{1}{2} \times 3 \times 1/8$ " were degreased, dipped in distilled water, and then suspended vertically. Using a small nasal atomizer, each was promptly sprayed with 2 ml of the water-displacing fluid. After drainage and evaporation of the solvent and water, the dry, film-coated specimens were tested in the fog cabinet at 100°F. Using this method, 2 percent by weight of ten different inhibitors were tested in 1-butanol, and the time required for first appearance of rust is shown in Table IX.

It is seen that glyceryl mono- and dioleate and sorbitan mono-oleate failed last (120 hours), while the first to fail (48 hours) were the amine nitrites, the dodecylammonium laurate, and the cyclohexylammonium 2-ethyl caproate. Apparently, any of the materials tested gives ample protection in the fog cabinet test.

C. Tests on Water-Soaked Electric Motor-Generators

Practical tests were conducted in which electrical equipment was submerged in synthetic sea water (Table X) for several hours, after which the equipment was restored by using one of the water-displacing compositions described here. A motor-generator²⁴ was submerged in the synthetic sea water at approximately 75°F for one week. It was then removed and dipped three times successively (about five minutes each) in city water to wash away as much as possible of the inorganic salts. Excess water was then removed by blowing with compressed air for about ten minutes.

Using a power sprayer (of the type commonly used in service stations for spraying oil on automobile chassis and springs), the equipment was then sprayed with 800 ml of a solution consisting of 99.5 percent technical n-butanol and 0.5 percent by weight of a mixture of glyceryl mono- and dioleate. In order to speed the subsequent drying process, the motor-generator was then blown²⁵ with hot air for 30 minutes.

The carbon brushes in electric motors and generators wear excessively when returned to service after having been in prolonged contact with sea water. In order to prevent this, it was deemed advisable to install new brushes. Also, the lubricant, usually a sodium soap grease, is emulsified and/or dissolved when in contact with sea water. Hence, the bearings were cleaned and repacked with new grease before returning the equipment to service.

²² Cf. footnote 3, page 2.

²³ H. R. Baker and D. T. Jones, "The NRL Fog Cabinet, the Army and Navy Aeronautical Specification Humidity Cabinet and their use in testing and rust inhibition of lubricants and rust preventives," NRL Report No. C-3100, July 1947.

²⁴ Type ZD (115-volt, a-c motor and 30-volt, 10-ampere, d-c generator) made by the Diehl Manufacturing Company, Elizabeth, New Jersey.

²⁵ Using "Heat Gun", Type C, made by Black and Decker Manufacturing Company, Towson, Maryland. Maximum air temperature: 200°F.

TABLE X
Composition of Synthetic Sea Water

A. Preparation of Stock Solutions for Synthetic Sea Water

Stock Solution No. 1

$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	3889.2 gms
CaCl_2 (anhydrous)	405.55 "
$\text{Sr Cl}_2 \cdot 6\text{H}_2\text{O}$	14.79 "
Dissolve and dilute to seven liters	

Stock Solution No. 2

KCl	486.15 gms
NaHCO_3	140.73 "
KBr	70.35 "
H_3BO_3	19.04 "
NaF	2.10 "

Dissolve and dilute to seven liters

B. Preparation of Synthetic Sea Water

NaCl	245.34 gms
Na_2SO_4	40.94 "

Dissolve in a few liters of water

Stock solution No. 1 200 ml.

Stock solution No. 2 100 ml.

Dilute to ten liters and adjust the pH to 8.2 with 0.1 normal Na_2CO_3 .
Only a few milliliters of the carbonate solution will be required if pure chemicals are used.

Resistance readings between the armature and ground, and between field coil and ground were taken and compared with those taken before submersion. Since the readings made after restoration were not unduly lower than the original readings, the motor was started at a low voltage and allowed to run. The voltage was increased slowly so as to warm up the armature and field coils gradually and to hasten the evaporation of the butyl alcohol-water mixture. Within one hour the voltage had been raised to normal. The motor generator was then allowed to run for 48 hours under its rated load of 150 watts. At this stage of the test the resistances had returned to within 10 percent of those noted before submersion. The equipment was stored for six months, and it was then found that no significant rusting had occurred. Insulation was in good condition. The motor-generator was operated satisfactorily at this time and again after storage for a year and a half.

The same reclaiming procedure was used on a motor control²⁶ and another motor-generator²⁷ outfit. They were immersed in sea water for a week, removed and washed three times successively with fresh water, blown with air, sprayed with the same water-displacing fluid, and dried with the hot-air blower.

It is interesting to note that while checking the resistances prior to assembly for operation it was discovered that a 550-ohm resistor in the motor control gave a reading of 40,000 ohms. On further examination an air hole was found to extend from the outer surface through the pitch coating and insulating material to the core of the resistor. Through this opening sea water had come into contact with the fine resistance wire and corroded it so badly that it had been severed in several places. The resistor was replaced and the assembly was started and allowed to run for 48 hours as previously described. The entire outfit was again immersed in sea water for one week and was then reclaimed without any trouble. Thus, in order to use this material, the equipment must be in at least mechanical working order at time of recovery. After storage for six months no serious rusting had occurred and the apparatus operated normally. And it was still operating satisfactorily after storage for a year and a half.

D. Discussion of Commercially Available Fluids

In the past two years the number of commercially available water-displacing fluids passing Specification 52-C-18 Grade III has increased from two to seventeen. These are being produced by twelve different manufacturers. Some of the analytical data available on these products as of June 1948 are summarized in Table XI. The flash points of five fluids are below 120°F, four are above 125°F, while the average flash point is 122°F. All but three fluids have pour points below -20°F. Except for one fluid, the percentage of volatiles is between 60 and 81 percent, the average being 70 percent. The percentage of nonvolatile material varies

²⁶Designated "Marine Control" (1.5 HP, 115 volts dc) and made by Cutler-Hammer, Inc., Milwaukee, Wisconsin.

²⁷Type H (115-volt, d-c motor and 1-K, 115-volt, a-c generator) made by Allis-Chalmers Manufacturing Company, Milwaukee, Wisconsin.

TABLE XI

Some Physical Properties of Commercial Water-Displacing Compositions*
(Bureau of Ships Specification 52-C-18 Grade III)

Manufacturer	Flash Point °F (°C)	Thickness of film (inches)	Nonvolatile material	Volatile solvent	Sp. gr. 60°F	Ash %	Lead %	Neutralization number	Saponification	B.P.	Distillation		Aniline point °F	Sp. gr. solvent
											50%	95%		
A	125 -30	.0003	30.97	69.03	0.823	0.05	none	0.60	11.45	306	314	374	134	0.785
B	130 -30	.0002	28.50	70.50	0.830	0.34	---	1.44	12.32	312	318	380	135.5	0.788
C	130 -30	.0003	33.06	66.94	0.876	1.64	0.56	3.40	16.90	314	320	348	132	0.764
D	115 -20	.0002	23.30	76.70	0.826	1.71	none	0.53	5.76	300	318	370	145	0.766
E	135 -30	.0003	37.94	62.06	0.867	2.26	1.13	7.29	---	298	320	---	---	---
F	120 -20	.0001	18.76	81.24	0.816	0.87	---	5.04	20.16	299	314	348	150.5	0.787
G	130 -20	.0003	36.73	63.27	0.842	1.77	0.30	1.13	---	308	318	354	143	0.786
H	125 -30	.0003	34.26	65.74	0.836	1.90	0.66	2.90	3.20	304	314	362	138	0.783
I	115 -0	.0002	28.83	70.17	0.836	0.31	none	0.06	1.22	300	310	322	121	0.787
J	125 -0	.0002	30.14	69.86	0.833	0.38	none	0.28	2.00	304	316	348	124	0.764
K	120 -20	.0002	27.34	72.66	0.845	1.85	0.35	---	---	204	312	326	133	0.801
L	120 -40	.0002	18.96	81.04	0.808	1.03	---	0.44	4.01	304	320	343	---	0.768
M	125 -30	.0002	28.75	71.25	0.829	1.04	none	0.26	4.70	300	316	352	131	0.766
N	110 -30	.0003	37.55	62.45	0.843	0.54	none	1.95	4.33	300	313	364	133	0.766
P	115 -30	.0002	29.41	70.59	0.905	0.10	---	3.83	46.00	298	310	334	2	0.807
Q	105 -30	.0003	20.50	79.50	0.819	0.42	---	0.10	1.10	278	292	412	115	0.836
R	130 -30	.0003	54.62	45.38	0.834	0.45	---	0.02	2.80	290	320	---	117	0.863

* These data were made available through the cooperation of W. B. Eells of the Naval Engineering Experiment Station, Annapolis, Md.

from 18 percent to 55 percent, the average being 30 percent. This is to be contrasted with the new fluids described here which contain approximately 1 percent of nonvolatile matter. The percentage of ash varied from 0.05 to 2.3 percent with an average of 0.9 percent. The neutralization number varied from 0.05 to 7.3 with an average of 1.8. The saponification number varied from 1.0 to 46.0, but the results are so widely distributed as to make an average of little use. It is difficult to say much about the nature of the nonvolatile constituents from these data. Values of the neutralization number may be influenced by the presence of many other compounds besides acids, such as heavy metal salts of organic acids, phenols, and readily saponifiable esters.

From the data available on percent ash, percent lead, neutralization number, and saponification number, it is concluded that the rust inhibitors and other polar compounds present in these fluids are one or more of the following high-molecular-weight materials: Sodium petroleum sulfonates, esters of fatty acids, or soaps of carboxylic acids derived from fatty acids or from petroleum acids. The specific gravity of the solvent varied from 0.76 to 0.87, but all except three were under 0.80. At 60°F the specific gravity of the entire composition varied from 0.81 to 0.90. From the data on the distillation, aniline point, and specific gravity of each solvent, it is concluded that all the solvents used are essentially aliphatic hydrocarbons in the Soddard solvent range, except in those compositions supplied by manufacturers designated in Table XI as P, Q, and R which contain some aromatic hydrocarbons. P being the most aromatic.

Measurements were made of the water-displacing ability of each of these fluids employing the water-displacement test described in Section IIIR. Not one of the commercial fluids was able to displace from steel a 2-ml layer of water. With a 1-ml layer, only fluid K (Table XI) was able to effect the small water displacement of from 1/2- to 3/4-inch diameter.

Because of its insolubility, a little talc spread upon the surface of water is useful in observing the spreading of films such as used here. Each of the seventeen fluids caused rapid formation of a film on water which readily pushed talc particles away from the point of impact of the test drop. Evidently, all but one of these fluids are too insoluble in water to displace more than an extremely thin layer.

These commercial fluids were developed primarily as rust-preventive compositions, and the high percentage of nonvolatiles (30 percent on the average) and the residual film of from 0.0002- to 0.0003-inch thickness (see Table X) are necessary to give to steel high resistance to weathering. It is not surprising that they are inefficient water-displacing fluids. It is believed that a separate specification is needed for water-displacing fluids of high water-displacing ability. The fluids developed here are intended primarily to get optimum water-displacement and the minimum non-volatile residue consistent with reasonable rust prevention. The residual coating will, therefore, not give steel or iron as high resistance to severe weathering as the 52-C-18 Grade LII fluids. It is possible, however, to increase the percentage of rust-inhibiting solute in the recommended fluids and thus to increase considerably the protection against weathering.

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V. SUMMARY

- (a) The basic principles of operation of water-displacing and rust-inhibiting fluids have been outlined. This has permitted the development of more effective water-displacing fluids.
- (b) A number of new classes of water-displacing fluids have been prepared, and laboratory measurements have established their superiority over available fluids.
- (c) A suitable method has been devised to salvage submerged equipment (electric motors, starters, generators) without dismantling or disassembling it. In general, however, it will be advisable to replace carbon brushes and regrease ball bearings.
- (d) In order for this method to be effective, it is essential that apparatus be capable of withstanding the attack of seawater in the absence of air and be mechanically workable at the time of the reconditioning procedure.
- (e) The new fluids recommended are not intended to serve equally well every purpose for which Specification 52-C-18 was written. Except in emergencies, they should be used only where highly effective water-displacement is needed. They have the disadvantage of higher cost than the 52-C-18 fluids and so are not recommended for use where a rust-preventive coating is the principal requirement.

VI. RECOMMENDATIONS

- (a) The method herein described for reclaiming submerged electrical and mechanical equipment should be given full-scale tests where facilities are available for submerging, washing, spraying, drying, and then operating the equipment. A variety of equipment embodying different types of construction should be used for these tests.
- (b) It is recommended that, in first tests, attention be directed toward compositions using fluids 1, 2, 3, 7, and 8 of Table VIII.
- (c) It is recommended that, before formal adoption of any of these new fluids, the Bureau of Medicine and Surgery be requested to evaluate the comparative health hazards of the new solvents and of those used in present Specification 52-C-18 compositions.
- (d) The displacement test on a 1-mm water layer on steel and the method of measuring equilibrium spreading pressure of the solvent are recommended as tests for both the Specification 52-C-18 Grade III liquids and the new fluids.
- (e) If the fluids described here prove more effective and more practicable in water-displacement than the present Specification 52-C-18 fluids (purchased as "Compound, Rust Preventative, Thin-Film"), it is recommended they be purchased through a new specification, "Compound, Water-Displacing."

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--
-- WITH SMALL CONCENTRATIONS OF RUST INHIBITORS OF THE POLAR TYPE IN
-- ORDER TO IMPROVE PROTECTIVE AND RUST-PREVENTIVE PROPERTIES.
-- FINALLY, ADDITION OF TRACES OF ANTIOXIDANTS IS SHOWN TO BE
-- EFFECTIVE IN GIVING AN INCREASED STORAGE STABILITY TO THE FLUIDS.
-- COMPARISONS ARE GIVEN OF THE NEW FLUIDS WITH THE COMMERCIALY
-- AVAILABLE MATERIALS. APPLICATIONS TO THE RECONDITIONING OF
-- ELECTRIC MOTORS, GENERATORS, AND STARTERS ARE DESCRIBED, AND A
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