

UNCLASSIFIED

AD NUMBER
AD151053
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; Mar 1958. Other requests shall be referred to Aeronautical Systems Div., Materials Lab., Wright-Patterson AFB, OH 45433.
AUTHORITY
AFAL ltr dtd 17 Aug 1979

THIS PAGE IS UNCLASSIFIED

AD0151053

WADC TECHNICAL REPORT 53-83

PART VI

ASTIA DOCUMENT No. 151053

DO NOT DESTROY
RETURN TO
DOCUMENTS CONTROL
BRANCH --- WCOSI
FILE COPY

CATALOGED BY WCC

33,604.

DEVELOPMENT AND EVALUATION OF HIGH TEMPERATURE GREASE THICKENERS

JOHN C. GOOSSENS

STANDARD OIL COMPANY (INDIANA)

MARCH 1958

This report is not to be announced or distributed
automatically in accordance with AFR 205-43A,
paragraph 6d.

Statement C
U.S. Govt and Their Contractors

WRIGHT AIR DEVELOPMENT CENTER

20030213118

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

- - - - -

Qualified requesters may obtain copies of this report from the ASTIA Document Service Center, Knott Building, Dayton 2, Ohio.

- - - - -

Copies of WADC Technical Reports and Technical Notes should not be returned to the Wright Air Development Center unless return is required by security considerations, contractual obligations, or notice on a specific document.

WADC TECHNICAL REPORT 53-83

PART VI

ASTIA DOCUMENT No. 151053

DEVELOPMENT AND EVALUATION OF HIGH TEMPERATURE GREASE THICKENERS

JOHN C. GOOSSENS

STANDARD OIL COMPANY (INDIANA)

MARCH 1958

MATERIALS LABORATORY

CONTRACT No. AF33(038)-23687

PROJECT No. 3044

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by the Research Department of Standard Oil Company (Indiana) under USAF Contract No. AF33(038)-23687. The contract was initiated under Project No. 3044, "Aviation Lubricants," Task No. 73310, "Aircraft Lubricating Greases." The work was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Lt. D. Kjerland and Mr. H. Schwenker acting as project engineers.

This report covers the work done by the author from October 10, 1956, to October 10, 1957, under the supervision of Messrs. R. S. Barnes, Group Leader; L. C. Brunstrum, Section Leader; and A. W. Lindert, Assistant Division Director.

ABSTRACT

This work was directed toward the development of new grease thickeners operable at temperatures above 450°F and as high as 700°F. During this period a variety of substances were prepared and tested as thickeners for silicone and ester fluids. Those which proved to be effective thickeners in less than 40% concentration were given preliminary screening tests and the better samples were run in the ABEC-NLGI bearing tester.

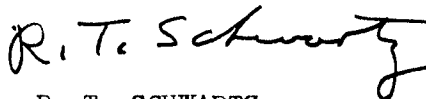
The general types of materials tested as high temperature thickeners were polar organic compounds, polymers, and organo-metal compounds. Selection of materials for test was based on thermal stability, ease of preparation, and ability to prepare the substance in small particle size. Of the many materials tested, those which have shown the greatest promise are, in decreasing order of their effectiveness, a new substituted pteridine, derivatives of hydrazine with bitolylene diisocyanate, phthaloyl melamine and some derivatives of cyanuric acid. However, at present none of these appears as good a high temperature thickener as the arylureas developed previously.

In addition to the usual 450°F high-speed bearing tests, 600°F bearing tests were conducted on silicone greases thickened with the two better thickeners, arylurea and a pteridine derivative. The tests were run both in air and under a slow stream of nitrogen. Both greases ran 85 to 120 hours under nitrogen. In air the arylurea had better oxidative stability running 40 to 60 hours in contrast with approximately 20 hours for the pteridine thickened grease.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



R. T. SCHWARTZ
Chief, Organic Materials Branch
Materials Laboratory

TABLE OF CONTENTS

	<u>Page</u>
Introduction	1
Hydrazine Derivatives	2
Pteridine Thickeners	4
Derivatives of Cyanuric Chloride	8
Evaluation of Commercial Solids as Thickeners	10
Dimethyl Sulfoxide-Isocyanate Reaction Products	11
Melamine-Dimethyl Sulfoxide Thickener	13
Miscellaneous Reactions and Thickeners	14
Reactions Involving Isocyanates	15
Reactions Involving Melamine	15
Substituted Ureas	16
Derivatives of an Anthracene Adduct	17
Alkylpyridine Oxidation Products	18
Salts of Maleic Acid Monoamides	18
Ferric Oxide-Amine Complexes	18
Bearing Test Program	19
Evaluation of Additional Fluids	22
L-41 Free Water Corrosion Test on MLG-9379	24
Silicone Grease Improvement Studies	25
Discussion	25

DEVELOPMENT AND EVALUATION OF HIGH TEMPERATURE GREASE THICKENERS

INTRODUCTION

Recent technological advances in the design of aircraft and weapons will require new lubricants which must be able to withstand very high operating temperatures as well as perform at very low temperatures. The upper temperature limit for long-service grease lubrication as determined by the current availability of suitable greases, is about 350°F for sliding-friction applications and about 450°F for lightly-loaded, ball-bearing applications. The present supplemental agreement under Contract No. AF33(038)-23687 is aimed at extending these temperature limits by the development of new grease thickeners for use at temperatures above 450°F.

Thickeners were synthesized and evaluated for use in greases for temperatures as high as 700°F. Because fluids suitable for use at such elevated temperatures were not available, this work was guided by a knowledge of the general requirements deemed necessary for a good high temperature thickener. The following are the properties generally accepted as being of the most importance:

- (1) Small Particle Size--The ideal size range may vary for each class of material, but in general, an effective thickener usually lies between 0.05 and 5 microns. Although important, the effects of particle size distribution and of particle shape are less understood.
- (2) High Melting Point--Melting point and temperature of decomposition should be well above the normal highest operating temperature of the grease.
- (3) Thickening Ability--The material should thicken oil to the desired consistency when used in concentrations below 35% and preferably below 20%.
- (4) Stability--The material must resist thermal decomposition, oxidation, mechanical break-down, agglomeration and changes of particle size or crystal modification.
- (5) Chemical Inertness--The material and its decomposition products should be noncorrosive to common bearing metals and nonreactive with the lubricating fluid over the desired temperature range.

Manuscript released by author December 20, 1957
for publication as a WADC Technical Report

- (6) Compatibility With the Oil--The material must be sufficiently oleophilic to form and maintain a homogeneous dispersion with the lubricating oil.
- (7) Rheological Properties--The thickener should be capable of producing a grease which resists changes in consistency under severe mechanical working.

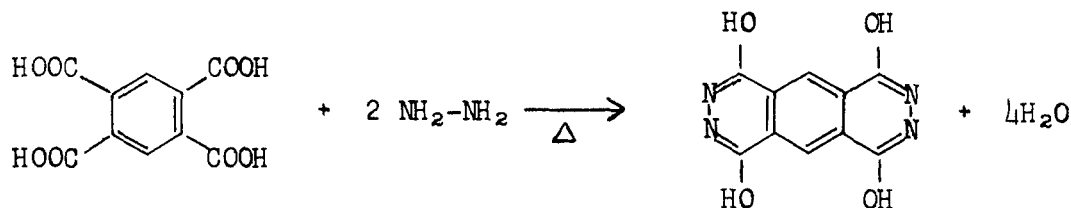
New organic compounds and those reported in the literature which possess melting points over 600°F and that can be prepared relatively easily from available starting materials were prepared for screening as potential thickeners. In the preliminary screening, the amount required to thicken DC-550 Silicone Fluid and a typical ester fluid to an NLGI No. 1 and 2 consistency and the effect of elevated temperatures on evaporation and consistency before and after mechanical working of the grease were determined. Those thickeners that appeared promising in the screening tests were tested in high-temperature bearing tests.

Thickeners studied during this year can be classified as follows: (1) hydrazine derivatives; (2) substituted pteridines; (3) derivatives of melamine and cyamuric acid; (4) reaction products of dimethyl sulfoxide; and (5) miscellaneous high melting organic compounds. Generally, purely organic materials possessing high molecular weight and thermal stability have proved to be the best thickeners.

Supplementary research was carried out on the following related subjects. A few experimental polyester and silicate ester fluids were evaluated for high temperature use. A study was made on the use of various rust preventives in MLG-9373, an arylurea-polyester grease, for the purpose of effectively inhibiting this product to pass the free water corrosion test. Two grease fillers, a dispersant and teflon, were also tested.

HYDRAZINE DERIVATIVES

High melting compounds for test as grease thickeners were prepared by use of reactions involving hydrazine. Thus, pyromellitic acid was reacted with an excess of aqueous hydrazine to form the dihydrazide which melts with decomposition at 840°F.



The pyromellitic acid was dissolved portionwise in aqueous hydrazine and the mixture was heated to dryness. The crude product was heated at 250°F until the ammonia-like odor no longer persisted. The compound proved insoluble in ordinary organic solvents and 200 ml of hot dimethyl sulfoxide was required to dissolve 5 g of the orange solid. Precipitation of the dihydrazide in fine particle size was accomplished by rapidly diluting this solution in cold water. The material was difficult to filter and proved oleophobic toward DC-550 Silicone Fluid.

Hot concentrated sulfuric acid was found to be an effective solvent for the dihydrazide without having the common disability of decomposing the material. The product was readily precipitated by pouring the dark orange acid solution into a rapidly stirred water-ice slurry. The solid again proved oleophobic toward silicone and ester fluids even when thoroughly washed with alcohol and acetone to remove traces of acid and water.

The reaction of bitolylene diisocyanate (TODI) with hydrazine and phenylhydrazine were carried out to produce high melting products suitable for use as grease thickeners. Hydrazine (64% in water) was reacted with TODI in dioxane to give an amorphous white solid, probably polymeric in nature. It had no melting point, but underwent slow thermal decomposition at 700°F. A portion of the dried material was tested at 21% concentration in DC-550 fluid, to give a grease of 357 penetration. Use of the undried material gave a grease of 304 penetration with only 20% thickener. These greases were given preliminary screening by successively heating them at 450°F for three hours and then remilling.

A third grease was prepared from this thickener by an in situ method. The aqueous hydrazine was not miscible with dioxane, but did dissolve in isopropanol. Before using isopropanol in preparation of the thickener, its reactivity with TODI was investigated. An equal volume of the solvent was added to a solution of TODI in silicone fluid. The reaction as evidenced by precipitate formation was quite slow even when the mixture was heated to 180°F. Since the reaction of TODI with hydrazine is extremely rapid, use of isopropanol as a mutual solvent should not interfere with formation of the desired product. The in situ grease preparation was carried out by adding a solution of the hydrazine in isopropanol to a solution of TODI in the oil with both solutions at 160°F. An immediate heavy precipitate was formed with noticeable evolution of heat. Removal of the solvent gave a smooth grease of 284 penetration containing 21% thickener.

With phenylhydrazine no in situ grease preparation was attempted. A benzene solution of phenylhydrazine was added to an equimolar solution of TODI in benzene, and the precipitate which formed was collected and thoroughly washed with acetone. The undried thickener was milled into DC-550 Silicone Fluid to produce a grease of 308 penetration at 19% thickener concentration.

These greases were subjected to two successive oven screening tests with the following results:

TABLE I
Oven Screening Tests
(450°F for 3 hours and 3-roll mill)

Thickener	Penetration		
	Initial	After One Cycle	After Two Cycles
TODI-Hydrazine (dried)	357	390	394
TODI-Hydrazine (moist)	304	312	321
TODI-Hydrazine (<u>in situ</u>)	284	235	247
TODI-Phenylhydrazine	308	317	365

The grease prepared with the phenylhydrazine derivative underwent too much softening in this test and was given no further evaluation. The two greases prepared from the hydrazine derivative and which maintained good consistency were run in the 450°F bearing test. The one prepared from moist thickener failed after 192 hours' operation; the other ran 182 hours. Although the grease prepared by the in situ procedure appeared better in preliminary screening, its performance in the bearing test was comparable with the grease prepared from the moist thickener.

Because of the poor bearing tests TODI-hydrazine greases gave in comparison with arylurea greases, no additional work was carried out with this type of thickener.

PTERIDINE THICKENERS

The synthesis of pteridine derivatives reported previously had been done in dimethyl sulfoxide solution. This procedure is objectionable because it leaves traces of dimethyl sulfoxide in the final grease. At high temperatures this contaminant decomposes to form foul smelling products. A systematic investigation of solvents was made to find a suitable substitute. The substituted pyrimidine sulfate employed in the synthesis is not readily soluble in most organic solvents. A mixture of acetic acid and glycerine proved to be a fair reaction medium. Addition of triethylamine to the mixture greatly improved the yield.

This new method of synthesis provides improved yields over the preparation in dimethyl sulfoxide; however, neither the air-dried powder nor the moist, freshly synthesized pteridine derivative is directly suitable for use as a thickener. The dried material was required in 45% to 50% concentration to thicken ester and silicone fluids to No. 0 grade greases. The moist material was little better, requiring 35% to 40% of the thickener. Slightly better grease yields are obtained with silicone fluid. This may be due to the greater viscosity of the silicone fluid as compared with that of the ester fluid.

Since the pteridine nucleus is substituted with both amino and hydroxyl groups, it theoretically should dissolve in either strongly acidic or basic solutions. The readily prepared 2-amino-4-hydroxy-6,7-diphenylpteridine was tested. It did not dissolve in 10% hydrochloric acid solution. Concentrated sulfuric acid did dissolve the material, but apparently caused cleavage of the molecule since the substance recovered upon dilution was low melting.

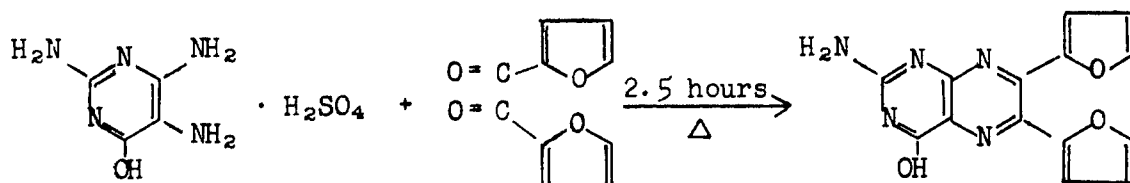
Dilute aqueous sodium hydroxide readily dissolved a small amount of the pteridine and addition of some alcohol to the solution substantially increased the solubility. Thus, an alcoholic potassium hydroxide solution was tested as a solvent, but only a small amount of material dissolved until water was added to the mixture. A dilute sodium or potassium hydroxide solution in a 20-80 mixture of water and ethanol proved to be the best solvent mixture for the pteridine. At 150°F, 20 g of the material was dissolved in 350 ml of solution and was reprecipitated with the calculated amount of acetic acid in 50 ml of alcohol. The precipitate was collected, washed liberally with acetone and used moist to prepare ester and silicone greases.

In comparison with the original method of preparing pteridine thickened grease, the new synthesis and reprecipitation procedure is a definite improvement. Better yield of the pteridine derivative is realized and less thickener is required to prepare a grease of any given consistency. Also the elimination of dimethyl sulfoxide eliminates objectionable odor from the grease.

In order to expand the study of pteridine thickeners, preparation of a new substituted benzil was attempted for reaction with 3,4,5-triamino-6-hydroxypyrimidine sulfate. A benzoin condensation was run on p-hydroxybenzaldehyde using the general method described in Organic Syntheses for benzoin itself. Without isolating the intermediate benzoin it was directly oxidized with nitric acid. This procedure produced an orange, water-soluble material, m.p. 230°-234°F, but none of the desired p,p'-dihydroxybenzil.

Similarly, a potassium cyanide catalyzed condensation of 2-furaldehyde was carried out according to the procedure described in the literature, J. Am. Chem. Soc., 33, 1228 (1911). A poor yield of furoin was obtained and subsequently this compound was oxidized in good yield to furil with copper sulfate in water-pyridine solution.

By heating the diketone with 2,4,5-triamino-6-hydroxypyrimidine sulfate for 2.5 hours in glycerol containing triethylammonium acetate, the desired pteridine derivative was produced.



The material remained unmelted at 690°F in a melting point capillary, but it began to darken above 620°F.

The thermally stable product was then tested as a grease thickener in DC-550 Silicone Fluid. The pteridine was dissolved in a dilute solution of sodium hydroxide in aqueous alcohol and reprecipitated with the calculated amount of acetic acid. The resultant fine precipitate was filtered through a Buchner funnel with considerable difficulty. While still moist the thickener was mixed into DC-550 fluid and the mixture was warmed to remove the volatile components. The material appeared somewhat oleophobic. As heating continued, the thickener coagulated to form a granular slurry with the oil. This unexpected result may have been due to improper washing of the precipitate prior to mixing it into the fluid.

The pteridine derivative was recovered from the unsuccessful preparation and reprecipitated from basic ethanol solution with the calculated amount of diluted acetic acid. As before, a very fine and difficult-to-filter product was formed. It was thoroughly washed with several portions of acetone and then mixed into DC-550 fluid. An excellent grease yield was obtained--223 penetration with 20% by weight of the pteridine derivative. The product was submitted to a three hour oven screening test at 450°F. It darkened more than expected, but it maintained its consistency well, softening from 223 to 231 penetration. This was too heavy for a bearing test so additional oil was blended into the grease to give a 268 penetration. In a 450°F bearing test this sample ran only 146 hours to failure. The bearing was still in good condition, but the grease was very tacky and heavy. Perhaps a softer preparation would run longer.

The pteridine thickener which has given the best results to date is that prepared from *o,o'*-dichlorobenzil. Another preparation of this material was made so that it could be incorporated into a DC-550 Silicone grease by use of the new precipitation procedure.

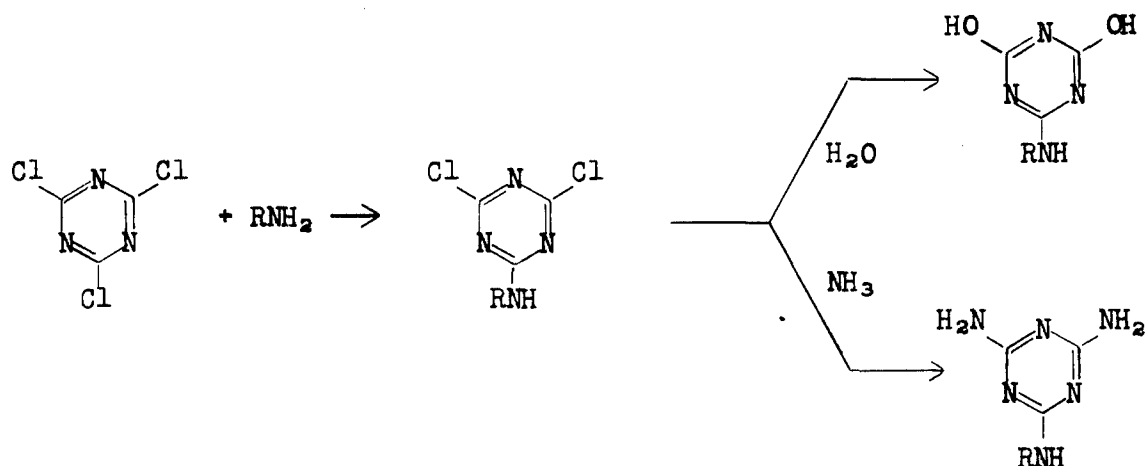
The *o,o'*-dichlorobenzil was prepared in an over-all yield of 38% from *o*-chlorobenzaldehyde as compared with only 23% previously obtained. This improvement was realized by use of copper sulfate in aqueous pyridine to oxidize the intermediate benzoin rather than a nitric acid oxidation. Preparation of the pteridine derivative in glycerin-acetic acid-triethylamine solvent proceeded rapidly and in good yield. The crude product was dissolved in a very dilute solution of sodium hydroxide in aqueous alcohol and heated with a few grams of decolorizing charcoal. The mixture was filtered to give a pale yellow solution and the pteridine was precipitated in fine particle size by stirring in a dilute solution of acetic acid sufficient to neutralize the base. After an acetone wash the moist precipitate was mixed into the silicone fluid. A grease of 373 penetration was produced with 26% thickener. This is a poorer grease yield than was obtained with the old preparation method.

Another reaction was carried out between 2,4,5-triamino-6-hydroxypyrimidine sulfate and *o,o'*-dichlorobenzil using glycerol containing triethylammonium acetate as the reaction medium. This product and the thickener recovered from the previous grease preparation were combined and dissolved in a dilute solution of sodium hydroxide in aqueous alcohol. The thickener was reprecipitated with acetic acid, collected on a Buchner funnel and washed liberally with acetone. Use of this moist product to thicken DC-550 fluid again produced a soft grease--337 penetration at 25% thickener concentration. After heating the grease at 450°F for three hours and remilling, it softened to a 355 penetration. This was somewhat better than the first preparation which gave a grease of 373 penetration with 26% thickener, but remained poor in comparison with the grease yields obtained using the old method of direct precipitation from the dimethyl sulfoxide reaction solvent.

A good grease yield was at last obtained in the next attempt. The soft grease from the previous preparation was directly dispersed and dissolved in sodium hydroxide solution with no attempt to remove the silicone fluid. Upon reprecipitation of the thickener with acetic acid, the flocculent precipitate gradually collected and separated with occluded silicone fluid into a soft mass. From this and some additional fluid an excellent pteridine thickened grease was obtained. At 20% thickener concentration, the grease had a 325 penetration. This grease, which is comparable in yield with those obtained by the old method, was run in a 450°F bearing test. It failed after only 94 hours in number 6 tester, which has been giving poor results. In tester number 1, this same grease ran 566 hours which is far superior to any test previously obtained with a pteridine thickened grease.

DERIVATIVES OF CYANURIC CHLORIDE

Cyanuric chloride is an inexpensive, reactive compound which can be used to prepare high melting derivatives of cyanuric acid and melamine.



By careful control of the reaction temperature, the chlorines of cyanuric chloride can be successively replaced to give mono-, di-, and tri-substituted products. Initially no attempt was made to limit the degree of substitution. Cyanuric chloride was heated in solution with an excess of various arylamines to obtain the tri-substituted melamine. Products of only moderate thermal stability were obtained. Thus, reaction with *p*-chloroaniline gave a crystalline solid which rapidly sublimed above 450°F without melting. Reaction with *p*-aminobenzoic acid yielded a product which melted with decomposition at approximately 600°F .

The chloride reacts less readily with substituted ureas and amides. The reaction product obtained with phenylurea in toluene solution melted below 450°F . Using acetamide a somewhat higher melting material was obtained, but it underwent severe thermal decomposition at 450°F .

Cyanuric chloride is only slowly hydrolyzed in hot water. Thus at room temperature it can be reacted with more active materials in the presence of water. An aqueous solution of sodium cyanurate was reacted with an equimolar portion of cyanuric chloride. The reaction proceeded rapidly with considerable evolution of heat. The white reaction product was not tested as a grease thickener since it was found to sublime readily above 500°F .

Cyanuric chloride was substituted in a stepwise manner by reacting it with an amine at controlled reaction temperatures. Partial reaction with an arylamine followed by total reaction of the remaining chloro groups with excess ammonia, is a suitable method for preparing aryl-substituted melamines. This general procedure was employed with α -naphthylamine and cyanuric chloride in toluene solution. When the reaction appeared complete after one hour, the fine white precipitate of α -naphthylamine hydrochloride was filtered off. The filtrate was then carefully mixed with an excess of concentrated ammonium hydroxide and the mixture was heated to promote complete reaction of the remaining chloro groups. Only a small amount of solid precipitated from the reaction mixture. This material did not melt or decompose, but approximately one half of the material sublimed on a hot plate at 550°F. The thermally stable residue was presumed to be the desired α -naphthylmelamine.

The reaction was repeated in an attempt to devise a method which would give a better yield. When toluene was employed as the reaction medium, a poor yield was obtained. Another run was made using acetone as the solvent. The amine hydrochloride formed in the initial reaction was not removed before the addition of excess ammonium hydroxide. The mixture was then heated to drive off the acetone and precipitate the product. When most of the acetone was driven off, more ammonium hydroxide was added and the mixture was heated again. The product obtained was soluble in hot acetone and melted below 300°F.

An attempted use of cyanuric chloride in dimethyl sulfoxide solution led to the discovery that these materials react quite vigorously with the release of hydrogen chloride. A study of this reaction with other acid chlorides showed that they also reacted with the sulfoxide to give the corresponding free acid. This type of hydrolysis reaction with dimethyl sulfoxide was noted previously in its reaction with phenylisocyanate, but was presumed to be due to the presence of water in the hygroscopic sulfoxide. However, the extremely vigorous reaction with acid chlorides such as benzoyl chloride and cyanuric chloride, which react sluggishly with water, indicates the hydrolyzing action is due not to the presence of water, but to direct reaction with dimethyl sulfoxide.

This reaction was applied to the preparation of a substituted cyanuric acid. By use of toluene as a reaction medium, cyanuric chloride was reacted with sufficient α -naphthylamine to replace one halogen. The precipitated amine hydrochloride was removed by filtration and excess dimethyl sulfoxide was added to the filtrate to convert the remaining halogens to hydroxyl groups. The product was separated from solution with water. It was dried and found to melt with decomposition above 500°F. The great thermal stability of cyanuric acid makes the poor stability of this derivative unexpected.

EVALUATION OF COMMERCIAL SOLIDS AS THICKENERS

Commercially available polyacrylamide has moderately good thermal stability. It is oleophobic toward mineral and silicone fluids. A portion of the polymer was heated in strong sodium hydroxide solution to partially hydrolyze the amide groups. This partial sodium salt was converted to the corresponding calcium and barium salts. These derivatives were gummy and could not be obtained in fine particle size suitable for use as a thickener.

Some derivatives of cyanuric acid were received from American Cyanamid Company for possible use in the development of high temperature thickeners. One sample, triallyl cyanurate, reportedly can be polymerized to a hard resin. Preliminary work involving peroxide catalyzed polymerization in benzene solution produced only a tacky sirup. A bulk polymerization of this material gave similar results.

At 20% weight concentration, dry sodium cyanurate powder was milled into DC-550 Silicone Fluid to produce a smooth grease of 317 penetration. However, due to the water solubility of this material, the grease structure readily broke down when the grease was mixed with water. In an attempt to overcome this disability, a portion of this material was converted to the corresponding calcium salt. Unfortunately, this salt came out of solution in large particles having little affinity for the oil, and formed only a granular slurry even after being passed over the three-roll mill.

A sample of melamine cyanurate powder had relatively poor thickening power and the resultant grease did not maintain its consistency when heated. Thus, a grease prepared from 42% of thickener in DC-550 fluid had a penetration of 223 but softened to 341 after being heated at 450°F for three hours. The material has excellent thermal stability as evidenced by virtually no discoloration during this treatment. It was found to be slightly acid soluble and a small portion of the solid was reprecipitated from hydrochloric acid solution. This product was apparently of finer particle size since it produced a grease of 360 penetration at 30% thickener concentration. Also, it was found to be quite soluble in strong base, so precipitation of the solid from sodium hydroxide solution was tried as a method for preparing it in fine particle size. A portion of the material was dissolved in aqueous sodium hydroxide and precipitated with dilute acetic acid. The melamine cyanurate was collected and washed successively with water and acetone before it was mixed into DC-550 Silicone Fluid. It exhibited little affinity for the oil. Removal of the excess solvent produced a grainy paste which milled to a smooth, heavy grease of 243 penetration with 30% thickener. This sample had poor stability to heat. In the oven screening test it softened to 320 penetration.

DIMETHYL SULFOXIDE-ISOCYANATE REACTION PRODUCTS

In the course of using dimethyl sulfoxide as a reaction solvent, it was observed that TODI produced an orange color when dissolved in this liquid. Colorless solutions were obtained when TODI was dissolved in other solvents. To determine if the color was due to an incipient reaction, a solution of TODI in dimethyl sulfoxide was heated under reflux and a heavy precipitate formed within a few minutes. The product was thermally stable, decomposing slowly without melting above 600°F. Additional investigation demonstrated this to be a general reaction between mono or diisocyanates and dimethyl sulfoxide.

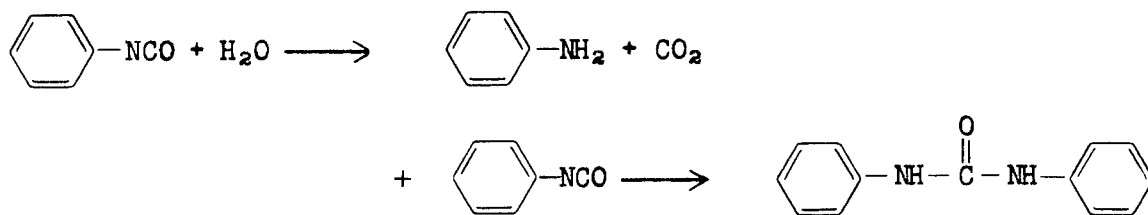
In an effort to determine the nature of this reaction the simple phenylisocyanate-sulfoxide product was prepared. It was a white crystalline material (m.p. 458°-460°F). The analytical data for this and the polymeric product obtained with TODI show little or no sulfur in the product. Thus, during reaction a sulfur-containing portion is split out. A simple dimer or polymer of the isocyanate is ruled out by the difference between the observed analysis and the calculated analysis for the two isocyanates used. This becomes more evident with the less complex phenylisocyanate product.

TABLE II

Elemental Analyses of Isocyanate-Sulfoxide Products

	<u>S</u>	<u>C</u>	<u>H</u>	<u>N</u>
TODI-DMS Product	0.45	72.23	6.12	9.54
TODI (calculated)	0.00	72.71	4.57	10.60
Phenylisocyanate-DMS	0.01	73.93	6.58	13.11
" (recrystallized)	0.00	73.52	5.87	12.83
Phenylisocyanate (calcd.)	0.00	70.60	4.20	11.75
Diphenylurea (calculated)	0.00	73.55	5.70	13.20

Although these analyses do not correspond with the product of any one-step reaction which can be postulated, the product from phenylisocyanate definitely corresponds in analysis and melting point with diphenylurea (reported m.p. 464°F). This compound can be formed by partial hydrolysis of the isocyanate to give aniline which can then react with more isocyanate.



Dimethyl sulfoxide is known to be extremely hygroscopic and this could account for the presence of water in the reaction mixture. However, a study of the reaction of acid chlorides with dimethyl sulfoxide, discussed above in this report, indicates the reaction does not involve water.

The TODI-sulfoxide product was evaluated as a grease thickener. The material, freshly precipitated from the reaction solution by dilution with excess acetone, was mixed into DC-550 Silicone Fluid. After the grease was heat treated and milled, a smooth product of $\frac{1}{4}$ size penetration of 55 was obtained. It softened to a penetration of 82 and developed the bad odor of thermally decomposed dimethyl sulfoxide after only 3 hours heating at 450°F. Additional 450°F heating for 20 hours caused an increase in penetration to 88.

An attempted in situ preparation of TODI-sulfoxide thickened grease resulted in a very soft, foul smelling product. Complete removal of the residual dimethyl sulfoxide must be accomplished to produce an acceptable grease.

Milling 30% by weight of the dried product into DC-550 fluid, produced a heavy grease of 260 penetration. In the oven screening test (3 hours at 450°F) the grease darkened considerably and upon remilling had softened to a 306 penetration. Another grease, prepared from a freshly synthesized product which was thoroughly washed with methanol and used moist, had a penetration of 225 at approximately 26% thickener concentration. This grease leaked severely in the oven screening test, but the oil was reabsorbed as it cooled to room temperature. After it was re-milled this grease had a penetration of 284. Although the washed thickener gave little evidence of thermal decomposition, it exhibited no improvement in maintaining consistency during heat treatment.

Since TODI-sulfoxide thickener is probably just a polymeric hydrolysis product of TODI and is a less effective thickener than that prepared directly from TODI and water, no additional work was done with it.

MELAMINE-DIMETHYL SULFOXIDE THICKENER

The bearing test program discussed later in this report required a variety of test greases. For this reason, preparation of the melamine-dimethyl sulfoxide polymer, a promising high temperature thickener reported previously, was undertaken anew. Before preparing a test sample of this grease, a preliminary investigation of the effect of varying amounts of water in the reaction medium was made. Four reactions were run with 50 ml of dimethyl sulfoxide, 2 g melamine and 0.1 g benzoic acid as catalyst. In the first sample the solvent was dried with anhydrous magnesium sulfate and the other three samples contained 1, 2, and 4 ml of added water, respectively. All were maintained at a reaction temperature of approximately 250°F. The elapsed time to precipitate formation was noted in each case, but no strict relationship between this and water content was found. However, it can be stated that the presence of water generally leads to a longer reaction time. The precipitates from these reactions were collected, washed with acetone and mixed into DC-550 fluid. Each of them proved oleophobic to an equal degree, thus the presence of water during formation of the product probably is not the cause of the inconsistent results which have been obtained in the preparation of this grease thickener.

Because melamine is only moderately soluble in dimethylsulfoxide and the reaction is known to be acid catalyzed, it was decided to determine if the more soluble melamine acetate would give the same thermally stable product in this reaction. In 50 ml of solvent and 1 ml of glacial acetic acid, 2 g of melamine acetate was heated to give a heavy gelatinous precipitate in 1.5 hours. This is only about a third the time ordinarily necessary to complete the reaction when melamine is employed. The product had the same physical appearance and thermal stability as that obtained by the former procedure. When tested as a thickener in DC-550, the precipitate was only mildly oleophobic and gave a very soft grease.

This modified procedure for the preparation of melamine-dimethyl sulfoxide thickener appeared superior to the old method so it was used on a larger scale in an attempt to prepare a grease. A round-bottom flask containing 250 ml dimethyl sulfoxide, 15 g melamine acetate and 20 ml glacial acetic acid was heated in an oil bath at 320°F. A heavy white precipitate had formed after two hours. The mixture was cooled to room temperature, diluted with acetone and the spongy solid was collected. Before the thickener was mixed into the oil it was leached with boiling acetone for $\frac{1}{2}$ hour in an effort to remove the occluded sulfoxide. Initially a very heavy, dry paste was formed. As the mixture was heated to drive off the excess solvent, it became progressively softer until a thin slurry resulted. Passage of this over a 3-roll mill did not improve the consistency. The entire preparation was repeated as described with the exception that only half as much oil was used in the grease mixture. However, when the residual solvent was removed, a slurry developed again.

The next reaction was run according to the procedure which had previously given an oleophilic thickener. A 10 g portion of melamine, 200 ml dimethylsulfoxide and 0.2 g benzoic acid catalyst were heated at 340°F with an oil bath. After ten hours a heavy precipitate of the polymeric thickener had formed and the mixture was cooled. The spongy, white precipitate was collected, washed and mixed into DC-550 fluid as before to produce a dry, mealy paste. The residual solvent was driven off leaving a soft, grainy mass which milled to a very soft grease of over 400 penetration. Weighing by difference indicated 14.2% thickener. Previously a good grease was obtained with as little as 10% of this thickener. This procedure was repeated with the exception that the reaction mixture was heated an hour after precipitation formation resulted. A better yield of thickener was noted, but this material was also very oleophobic.

The melamine-sulfoxide thickener from these unsuccessful preparations was separated from the oil, washed thoroughly with acetone and air dried at room temperature. It was then tested as a thickener in DC-550 fluid at 40% concentration. The heavy mixture was milled and heated at 450°F for two hours. A dry, crumbly mass of very bad odor resulted. Apparently traces of occluded sulfoxide still remained. This was remilled to a semifluid. After it was heated at 450°F for another 5 hours, it once more became very dry and milled to a slurry. Thus, this oleophobic product is worthless as a grease thickener even in high concentration.

Finally a method was developed which gave an oleophilic thickener. The procedure was as described above except that after the precipitate had been thoroughly washed with water and acetone, it was heated in a large volume of xylene. This drove off the volatile components as was evidenced by the rise in the temperature of the boiling mixture. During a 0.5 hour period the temperature rose from 170° to 270°F. The white, spongy precipitate was collected on a Buchner funnel, sucked nearly dry and then mixed with DC-550 fluid. At 15% thickener concentration, a smooth grease of No. 2 consistency was obtained. This treatment must have removed the occluded sulfoxide sufficiently to render the material oleophilic. Unfortunately, this successful preparation was not obtained soon enough to evaluate in the high temperature bearing test program.

MISCELLANEOUS REACTIONS AND THICKENERS

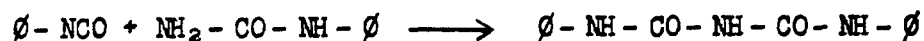
A number of high melting materials were tested as thickeners and some unsuccessful reactions were carried out in attempts to prepare such materials. It is difficult to classify these topics and most are not worthy of detailed discussion. For the sake of completeness, these are included here under the general heading of miscellaneous reactions and thickeners.

REACTIONS INVOLVING ISOCYANATES

Trioxane was heated with TODI in ethyl acetate solution containing a small amount of organic acid catalyst. It was hoped the reactants would form a thermally stable polymer which might be applicable to an in situ preparation if it proved to be a successful thickener. However, even after prolonged heating, no reaction was observed.

The thermal stability of silica thickened greases is dependent upon the stability of the organic coating used to render the silica hydrophobic. The organic coating is chemically bonded through the free surface hydroxy groups. An attempt was made to obtain a thermally stable coating by reacting the silica with phenylisocyanate. Both with benzene solvent and without solvent, no reaction could be detected and the silica residue, after it was heated to dryness, remained hydrophilic.

Biuret is a moderately stable compound which melts with decomposition at 378°F. In a manner analogous to substituted ureas, substituted biurets could be good high temperature grease thickeners. Reaction of an isocyanate with a mono-substituted urea would produce a disubstituted biuret.



Reaction of bitolylene diisocyanate (TODI) with phenylurea was carried out in hot xylene. The reaction proceeded very slowly to give a dark, gummy precipitate. Attempted reaction at a lower temperature in refluxing acetone gave no reaction.

REACTIONS INVOLVING MELAMINE

Melamine derivatives are often thermally stable and high melting; however, the general insolubility of melamine in organic solvents renders it difficult to react by solution methods which generally lead to finely divided products. In an effort to convert melamine to a soluble form, it was reacted with glacial acetic acid to yield a crystalline acetate. This material sublimed rapidly above 500°F without melting. It proved moderately soluble in hot xylene and was reacted with TODI in this medium. The high melting tan precipitate which gradually formed proved to be oleophilic toward DC-550 and ester fluids.

Equal weights of melamine and phthalic anhydride were intimately mixed and heated at such a temperature that the anhydride gradually sublimed. After several hours the temperature was increased to completely sublime the unreacted melamine and anhydride. A tan powder remained which was very stable to above 700°F. This same product could be prepared by

Urea reacts with malonic acid to produce barbituric acid. In a similar manner urea was reacted with other dibasic acids in an effort to produce some high melting cyclic or linear derivatives which might be used as grease thickeners. In most cases, poor yields were obtained and the products melted below 500°F. With oxalic acid a red substance was obtained which did not melt but readily sublimed above 500°F. None of these products was suitable for a high temperature thickener.

DERIVATIVES OF AN ANTHRACENE ADDUCT

The Diels-Alder adduct of anthracene with maleic anhydride, 9,10-dihydroanthracene-9,10-succinic anhydride, was prepared in xylene solution. A number of derivatives of this anhydride were investigated as possible high temperature grease thickeners.

The reactions between the adduct and ammonia and two arylamines produced derivatives which were too low melting to warrant further preparation of such materials. The observed melting points of these crystalline products are listed below.

TABLE III
Melting Points
of Anthracene Adduct Derivatives

<u>Reacting Amine</u>	<u>Melting Point of Derivative</u>
Ammonia	600°F
p-Toluidine	454°F
p-Chloroaniline	527°F

The sodium salt of the adduct was only slightly soluble in hot water and crystallized in fine white needles. A finely divided precipitate of the insoluble calcium salt was prepared and tested as a thickener. It was oleophilic and thermally stable, but a grease prepared with this material and DC-550 broke down to a slurry when subjected to the 450°F oven screening test.

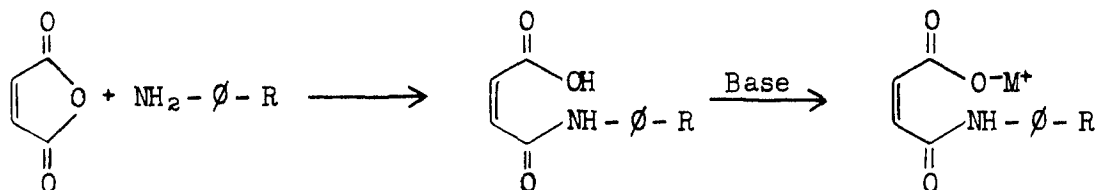
ALKYLPYRIDINE OXIDATION PRODUCTS

Some high melting derivatives obtained by the oxidation of alkylpyridines were investigated as high temperature grease thickeners. One sample which was neutral and of fine particle size was milled into silicone fluid. It required 40% by weight to produce a soft grease of 410 penetration. A second sample which was slightly acidic, was dissolved in hot sodium hydroxide solution and reprecipitated by pouring the solution into sufficient alcohol-acetic acid mixture to completely neutralize all the sodium hydroxide. A gelatinous, precipitate was formed which proved very difficult to filter. Even after thorough washing with methanol and acetone this material remained entirely oleophobic. Reprecipitation of this material from a potassium hydroxide-methanol solution gave analogous results.

SALTS OF MALEIC ACID MONOAMIDES

As previously reported, maleic anhydride reacts rapidly in solution with aromatic amines to form the corresponding monoamides. In most cases, these products were not sufficiently high melting to be useful as high temperature grease thickeners.

In order to increase the melting point of these maleic acid derivatives, a number of them were converted to sodium and calcium salts.



These salts proved to be thermally stable up to 550°-600°F. When screened as potential thickeners for DC-550, these materials all proved oleophobic both as freshly prepared moist precipitates and as the dried powder. Only soft, grainy greases resulted from milling 40% to 50% of these materials with oil.

FERRIC OXIDE-AMINE COMPLEXES

Three compounds of ferric iron were prepared and tested as high temperature thickeners. By treating a solution of hydrated ferric chloride in acetone with excess isopropylamine a heavy brown precipitate was formed. It was totally oleophobic and melted with decomposition above 500°F. A similar material prepared from ammonia had greater thermal stability, but was equally oleophobic toward silicone fluid.

A sample of ferric oxide was prepared by pouring an aqueous ferric chloride solution into a rapidly stirred, hot sodium hydroxide solution. The precipitate was heated in the boiling solution for a few minutes; then it was collected, washed with methanol and mixed into DC-550 fluid. The oleophilic oxide produced a heavy grease with approximately 18% thickener concentration. However, the product broke to a thin slurry when heated to 450°F for 3 hours.

BEARING TEST PROGRAM

In addition to usual bearing tests conducted at 450°F with experimental grease samples, a bearing test program was initiated during the last part of the contract period, for the evaluation of the better thickeners at 600°F. These high temperature tests were run on a Pope Company bearing tester purchased with government funds. The test instrument was modified so that it could be run normally in air or under an inert atmosphere which, in this case, was nitrogen.

So that the greases tested would be comparable, all were prepared from DC-550 Silicone Fluid in small beaker batches and no additives were used. The first grease to be tested was MLG-9349. A 100 g sample was prepared using 16% thickener. The grease was heat treated at 450°F for three hours and then three-roll milled to give a smooth product of 304 penetration.

This grease was used to initiate the 600°F bearing test program. In air, it ran 62.5 hours to failure. Operation under an atmosphere of nitrogen was then begun. During the first test a nitrogen flow rate of approximately two liters per hour was used with the result that bearing failure occurred in 13.5 hours. Inspection of the test bearing indicated failure was due to removal of the lubricant by the stream of nitrogen rather than to decomposition of the grease. A second test with a nitrogen flow rate of 0.4 liter per hour ran 52 hours before failure and a third test with a flow rate of 0.1 liter per hour lasted 118 hours. Use of a slower flow rate was not practicable with the flow metering system which employed a Rotometer. A still slower flow rate or closed bearing housing possibly would give better results. In any case, use of an inert atmosphere substantially increased bearing life at high temperature.

Dual tests were run with this grease sample, in air and under an atmosphere of nitrogen, in order to check the repeatability of the test. These tests ran 41 hours in air and 86 hours under nitrogen as compared with 62.5 hours and 118 hours for the same tests run previously. This rather wide discrepancy demonstrates the need for running a number of tests in evaluating a particular grease sample, or in comparing two different thickeners.

The pteridine derivative which had given the best results in 450°F test work, 2-amino-4-hydroxy-6,7-di(o-chlorophenyl) pteridine, was used in a DC-550 grease to evaluate this type of thickener in 600°F operation. A rather soft sample of 325 penetration at 20% thickener concentration ran only 19.5 hours in air. It was not tested under nitrogen. A heavier preparation of the same grease, 284 penetration with 22% thickener, ran 24 hours in air and 91 hours under nitrogen. From these limited data, it can be judged that consistency differences in this range are not too important. In addition, the pteridine thickened grease appears more susceptible to oxidative degradation than does the arylurea thickened grease.

In Table IV are listed all the bearing tests which were run during the past year on experimental grease preparations. Generally, tester No. 1 gave the high results while tester No. 6 was most severe. The ASU thickener in each case is the aryl-substituted urea formed by the reaction of bitolylene diisocyanate (TODI) with equimolar portions of p-toluidine and p-chloroaniline. The greases prepared from pteridine derivatives were prepared by the method of precipitating the thickener from basic solution as already described.

Tests 1, 2, 3, and 4 were run on high temperature ester greases. These products do not have the necessary properties for low temperature applications; however, they might find limited use where a high temperature grease of high lubricity is required. These greases not only give good performance in the high temperature bearing test, but also do well in the Navy Gear Wear and Actuator tests where silicone greases fail completely.

Test No. 5 was a typical result on a small kettle batch of ASU-XF-258 grease which had been prepared in an attempt to develop a product meeting the requirements of MIL-G-25013A. A portion of this was submitted during March, 1957, for qualification against this specification with a request for waiver on the penetration requirement.

Tests 6, 7, 8, and 9 were run in order to evaluate a new silicone fluid developed by General Electric as a product equivalent to DC-550. The fluid designated GE 370-87-252 was an early pilot plant sample of GE-81705 fluid. The fluid used in test No. 7 had been improperly stripped of light ends and had a high evaporation loss. However, this does not appear to have adversely affected its performance when compared with tests 8 and 9 which were run on the stripped material.

The two tests run on grease samples prepared from Dow Corning Fluid XF-4039 are in good agreement. The sample prepared from 15% thickener was a small beaker batch made in the initial evaluation of this fluid. The other sample was prepared in a grease kettle and required 20% thickener to obtain a product of similar consistency.

TABLE IV

L-35 Bearing Test Results
(10,000 rpm)

Ref. No.	Grease		Weight Per Cent	Bearing Test	
	Fluid	Thickener		Spindle*	Hours Run
<u>Test Temperature 350°F</u>					
1	Drew's Polyester	Arylurea	12	3	785
<u>Test Temperature 400°F</u>					
2	Drew's Polyester	Arylurea	12	1	148
3	J-15 Ester	Arylurea	20	6	336
4	J-36 Ester	Arylurea	20	1	168
<u>Test Temperature 450°F</u>					
5	XF-258	Arylurea	20	3	300
6	GE-370-87-252	Arylurea	16	6	215
7	GE-81705	Arylurea	15	3	305
8	GE-81705	Arylurea	15	1	242
9	GE-81705	Arylurea	15	1	427
10	XF-4039	Arylurea	15	1	472
11	XF-4039	Arylurea	20	1	446
12	DC-550	TODI-Hydrazine	20	6	192
13	DC-550	TODI-Hydrazine (in situ)	21	6	182
14	DC-550	TODI- α -naphthylamine	14	6	115
15	DC-550	TODI- α -naphthylamine-p-toluidine	13	6	229
16	DC-550	<u>o</u> -chlorobenzil-pteridine	20	6	94
17	DC-550	<u>o</u> -chlorobenzil-pteridine	20	1	566
18	DC-550	Furil-pteridine	18	1	146
<u>Test Temperature 600°F</u>					
19	DC-550	Arylurea	16	Pope	62
20	DC-550	Arylurea	16	Pope	41
21	DC-550	Arylurea	16	Pope	118*
22	DC-550	Arylurea	16	Pope	86*
23	DC-550	<u>o</u> -chlorobenzil-pteridine	20	Pope	19
24	DC-550	<u>o</u> -chlorobenzil-pteridine	22	Pope	24
25	DC-550	<u>o</u> -chlorobenzil-pteridine	22	Pope	91*
26	XF-4039	Arylurea	20	Pope	42

* Numbered spindles are of ABEC-NLGI design

* These tests were run under nitrogen atmosphere

Tests 14 and 15 represent two modified arylureas which have superior thickening ability. Both bearing performance and objectionable odor removed these preparations from further consideration.

The greases thickened with pteridine derivatives were prepared by milling the freshly precipitated solid with DC-550 fluid, heat treating the product at 450°F and then remilling. It is difficult to account for the wide variation between tests 16 and 17 even when considering the greater severity of No. 6 spindle. The 566 hour test obtained with the pteridine grease is far superior to any previous test run on the same grease prepared by the old method employing dimethyl sulfoxide as the solvent. The pteridine derivative prepared from furil possesses excellent thickening power. Upon completion of this test the failed bearing appeared to be in good condition, but the grease had become very heavy and tacky. A softer grease sample would probably do better.

Tests 19 through 26 comprise the data obtained in the 600°F bearing test program. It was originally planned to test the three best high temperature thickeners in the same fluid both in air and under nitrogen. Inability to prepare a grease thickened with melamine-sulfoxide polymer before the end of the contract period, reduced this to testing of ASU and pteridine thickened greases only. At 600°F the ASU thickener will operate approximately the same length of time as the pteridine thickener under nitrogen. In air the ASU thickener has approximately twice the life of the pteridine derivative. The last test run with an ASU-XF-4039 grease shows that this new fluid has about the same high temperature stability as DC-550 fluid.

EVALUATION OF ADDITIONAL FLUIDS

A limited amount of evaluation work was carried out with some new high temperature fluids. Three of these were silicate esters, designated Silgon numbers 2, 3, and 4 by Anderson Chemical Company. At 450°F all three samples had completely decomposed after 18 hours.

An experimental silicone fluid, designated GE 370-87-252 by General Electric Company, was partially evaluated and appears comparable to DC-550 Silicone Fluid. It has a pour point of -40°F and is stable at 450°F. A small laboratory batch of grease was prepared from this fluid and 17% by weight of arylurea thickener. This grease failed the Navy Gear Wear Test under both the 5 and 10 pound loads. In a high temperature bearing test, it performed moderately well, failing after 215 hours in tester number 6.

An improved version of this fluid, GE-81705, was then received. This product is a methylphenyl fluid similar to DC-550. Preliminary tests with this experimental product proved it to be compatible with the arylurea

thickener used in MLG-9349. However, a 450°F evaporation test for 24 hours gave a 6.9% loss compared with 1.9% for a DC-550 sample used as a control. This high evaporation was due to some light ends, which had not been properly stripped out. A second sample of this fluid lost 3.05% by weight as compared with 3.2% for a control sample of DC-550. Bearing tests at 450°F were run on greases prepared from this fluid. They ran 242 hours and 427 hours.

Another experimental silicone fluid, XF-4039, was received from Dow Corning for possible use in a grease to meet with the MIL-G-25013A specification. Preliminary investigations with beaker preparations of grease using this fluid were encouraging. For this reason a 30 pound kettle batch of the grease was prepared using the present arylurea thickener. None of the difficulty experienced with kettle production of XF-258 thickened greases was encountered. The fluid possesses sufficient solvent power so that the grease can be prepared by the in situ method without solvent. At 20% thickener concentration and with 0.5% of Span 80 as the only additive, a smooth grease of 318 penetration was obtained. A number of tests have been completed on this formulation with the following results.

TABLE V

Test Results on ASU Thickened XF-4039

Drop Point	508°F
150 g Cone Penetration, unworked	318
worked 60 strokes	315
worked 100,000 strokes	311
Low Temperature Torque, -65°F	1 sec./rev.
Apparent Viscosity, -65°F and 20 sec. ⁻¹	2700 poises
Leakage, 30 hours at 350°F	5.45%
Evaporation, 22 hours at 400°F	1.8%
High Temperature Bearing Test, 450°F	472 hours
Navy Gear Wear Test, mg loss/1000 cycles at 5 lb.	6.8

A polyester fluid (MW-3992) submitted for our evaluation by E. F. Drew and Company has a rather high pour point, 0/20°F, but its reported high temperature stability is excellent. Evaporation loss during 22 hours at 400°F for this polyester was only 1.9% as compared with 2.8% Hercoflex 600, the ester fluid used in MLG-9373. A portion of the fluid was thickened with 12% by weight of arylurea to produce a grease of 311 penetration. This product ran 6250 cycles to failure in an actuator test (screw-in-nut; 350°F), and has given excellent results in 350° and 400°F bearing tests.

Two experimental pentaerythritol esters, J-15 and J-36 were supplied by the Hercules Powder Company. These are analogous to their Hercoflex 600 fluid, but with superior high temperature stability and higher pour point. Fluid J-36 has properties very similar to those of the Drew Company polyester fluid, while J-15 covers a somewhat higher liquid range. In a 400°F high speed bearing test a grease prepared from J-15 ester and 20% arylurea thickener ran 336 hours. Compared with 148 hours for Drew's polyester grease, a similar grease prepared from J-36 ran 168 hours.

L-41 FREE WATER CORROSION TEST ON MLG-9379

In cooperation with the Materials Laboratory of Wright Air Development Center, a number of tests have been completed on MLG-9373, an ester-arylurea grease. It gave excellent results in the conventional grease tests with the exception of the free water corrosion test. A number of standard rust preventives, such as Span 80, Pentamul 126, Ortholeum 162, and octenyl succinic anhydride (OSA), have been tested singly and in combination to improve the rust protection of the grease, but none provides sufficient protection to pass the test. The formulation, which gave by far the best results, incorporated the following amounts of additives: 0.5% Pentamul 126, 0.2% Ortholeum 162, and 0.2% octenyl succinic anhydride.

The Materials Laboratory of Wright Air Development Center suggested the use of an additive available from Universal Oil Products Company. A sample of this material, additive No. 2660-185, was obtained and evaluated as a rust inhibitor for MLG-9373. This additive gave encouraging results, but additional work will have to be done in order to determine the additive combination and concentration which is best.

TABLE VI

L-41 Free Water Corrosion Tests on MLG-9373

<u>Additive Formulation</u>	<u>Test Result</u>	<u>CRC Rating</u>
Blank	Failure	3
0.5% No. 2660-185	Failure	3
0.5% No. 2660-185 + 0.5% dimer acid	Failure	3
0.5% No. 2660-185 + 0.5% OSA	Borderline Failure	2
1.0% No. 2660-185	Borderline Pass	1

Each formulation was run in duplicate. Use of dimer acid with No. 2660-185 appears to be of little value although use of octenyl succinic anhydride gave only a borderline failure. With 1% of No. 2660-185 one bearing was entirely free of corrosion and the other had just one spot on one of the rollers.

This problem of MLG-9373 passing the free water corrosion test may be one of test procedure, because a recent report from Wright Air Development Center states that their laboratory has had passing results in this test using a sample of MLG-9373 containing no special rust preventives.

SILICONE GREASE IMPROVEMENT STUDIES

Two additives were evaluated for the general improvement of silicone based greases. First, the effect of a dispersant on the grease yield of fluids thickened with a high melting organic thickener was studied in the preparation of several beaker batches of MLG-9349. Small amounts of a thermally stable sulfonate detergent were added to the oil before the in situ formation of the thickener was carried out. The resultant greases were heat treated at 450°F for three hours and milled. Improvement of the grease yield based on the penetration values of these greases was inconclusive, although a slight improvement was noted.

Secondly, to determine if the use of Teflon powder as a filler in silicone grease would improve performance in the Navy Gear Wear Test, a sample of MLG-9349 was prepared containing 2% of Teflon. This experimental grease gave results comparable with those obtained by the unmodified grease. It gave a 4.9 mg loss per 1000 cycles under a five pound load.

DISCUSSION

Early work on the development of high temperature grease thickeners brought forth arylureas as good materials both from the viewpoint of ease of preparation and from the availability of chemicals. A great number of these compounds were screened before the present thickener, formed from bitolylene diisocyanate (TODI), p-chloroaniline, and p-toluidine was selected. Several other thickeners performed equally well, but with this choice continued availability of the ingredients was assured and manufacturing procedure was quite simple. When the project for development of a thickener stable to 700°F was begun, it became apparent a thickener other than an arylurea would be required, because all substituted ureas studied were found to undergo thermal degradation in the range 600° to 700°F.

The search for a good 700°F grease thickener is one which can be directed primarily by choice of materials having the necessary thermal stability. Other properties which a good thickener must possess are recognized, but are impossible to predict. At first, a survey of the literature was made to reveal readily accessible organic substances having melting points above 600°F. Such compounds are few in number, so considerable work had to be done in preparing new substances for test. Since there are few guides to direct a research program of this nature, the task of finding a good high temperature grease thickener is difficult and the approach is somewhat desultory.

In spite of these problems, the present studies have brought to light a few general rules which can be of value in the search for a good thickener. Potential grease thickeners must be sufficiently polar to maintain interparticle attraction and resist phase changes, yet not be so crystalline as to encourage formation in large particle size. Highly symmetrical molecules, while they tend to be thermally stable, are also prone to high crystallinity.

The use of polymeric substances as thickening agents is a promising approach to this problem. Resins which possess high melting points, thermal stability and lend themselves to formation in an appropriate particle size are generally superior in thickening ability to compounds having analogous but simpler structure. This may well be due to the typical lack of crystallinity exhibited by nonoriented synthetic polymers, and to their formation in particle shape which exposes a high surface area.

The new materials studied during this period which exhibited particular ability as thickeners were the reaction product of hydrazine with TODI, a new pteridine derivative, phthalic melamide, and certain derivatives of cyanuric acid. However, none of these is as good as the arylureas developed earlier. These and the other materials prepared for screening are tabulated with their properties and general effectiveness in Table VII.

The silicone grease which now appears best able to meet the requirements of a -65° to 450°F grease such as outlined by specification MIL-G-25013A, is one prepared with our current arylurea thickener and XF-4039 fluid. This silicone fluid is similar to XF-258 in stability and liquid range, but is superior in its general applicability to the manufacture of an arylurea-thickened grease. In bearing performance, DC-550 and XF-4039 greases are comparable. However, the low temperature properties of the latter are such that it is usable at 30°F lower than the DC-550 grease. As with other silicone greases, the XF-4039 grease has poor lubricity and cannot pass the Navy Gear Wear test.

TABLE VII

Materials Tested as Thickeners in DC-550 Fluid

Thickener		Melting Point, °F	Wt. % Used	Resultant Grease	
Material	Appearance			ASTM Pen.	450°F Performance
Pyromellitic dihydrazide	Orange powder	840	30	>400	-
Hydrazide of TODI	White powder	Dec. > 700	21	284	Very good
Phenylhydrazide of TODI	Tan powder	Dec. > 600	19	308	Good
o,o'-Dichlorobenzil pteridine	Yellow powder	> 700	20	325	Excellent
Furil pteridine	Green powder	> 700	20	223	Excellent
Tri (N-chlorophenyl) melamine	Crystalline	Sublimes 450	-	-	-
Tri (N-carboxyphenyl) melamine	Crystalline	Dec. > 600	35	>400	-
α -naphthyl melamine	Tan powder	> 700	35	340	-
α -naphthyl cyanurate	White powder	Dec. > 500	-	-	-
Cyanuryl cyanurate	White powder	Sublimes 500	-	-	-
Sodium cyanurate	White powder	> 800	20	317	Good
Calcium cyanurate	Crystalline	> 800	35	>400	-
Melamine cyanurate	White powder	> 700	30	243	Poor
Polyacrylamide	White powder	Dec. > 500	40	400	-
Sulfoxide-TODI product	Orange powder	Dec. > 600	26	225	Fair
Phthaloyl melamine	Tan powder	> 700	35	320	Good
Glyoxal-melamine resin	White powder	Dec. > 600	40	>400	-
Anthracene adduct derivatives from ammonia	Crystalline	Dec. > 600	-	-	-
from p-chloroaniline	Crystalline	527	-	-	-
calcium salt	White powder	> 700	30	290	Poor
Alkyl pyridine oxidation products					
neutral derivative	Black powder	> 800	40	>400	-
base soluble derivative	Black granules	> 800	-	-	-
Monoanilides of Maleic acid					
sodium salt	Crystalline	> 600	-	-	-
calcium salt	White powder	> 600	40	>400	-
Ferric oxide complexes					
with isopropylamine	Brown powder	Dec. > 550	40	>400	-
with water	Red powder	> 700	30	256	Poor

A series of 600°F bearing tests were run on a new Pope spindle both in air and under a slow stream of nitrogen. Previously, a few aryl-urea greases had been run in air at this temperature on the ABEC-NLGI testers with results in the 25 to 50 hour range. These new tests, on the average, ran longer--this may be due to a greater stability of the arylurea thickener now being employed. The spread in bearing test life between operation in air and under nitrogen is greater for the pteridine thickened grease. This indicates that arylureas are less susceptible to oxidative degradation at 600°F.