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NATIONAL DEFENSE RESEARCH COMMITTEE
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ALUMINUM CRESYLATE FROM PETROLEUM CRESYLIC ACIDS

BY

G.C. Brock and A.G. Orr
California Research Corporation

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ALUMINUM CRESYLATE FROM PETROLEUM CRESYLIC ACIDS

Service Directive: CWS-10

Endorsement (1) from Dr. H.C. Hottel, Chief, Section 11.3 to Dr. H.M. Chadwell, Chief, Division 11.

Forwarding report and noting:

"Near the end of the war there was considerable interest in liquid agents for making gelled fuels for flame throwers and blaze bombs. This report describes one of the more promising of these liquid thickening agents. Aluminum cresylate solution mixed with a fatty acid solution in a two-stream method, producing aluminum soap in situ, provides a convenient continuous process for making gelled fuels."

Endorsement (2) from Dr. H.M. Chadwell, Chief, Division 11 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee.

Forwarding report and concurring.

This is a progress report under Contract OEMsr-1468 (11-512) with the California Research Corporation.

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TABLE OF CONTENTS

SUMMARY

1. The problem assigned was to determine if petroleum cresylic acids were suitable for the manufacture of aluminum cresylate used for "in situ" formation of gasoline gels in incendiary bombs and flame-throwers.

2. Preliminary work was directed toward comparative tests on materials prepared from both coal tar and petroleum derived acids. These experiments showed that the source of the cresylic acids had no effect on the properties of the corresponding aluminum salt but that boiling range and contaminants were the properties to be considered.

3. Gel preparations with various types of aviation gasoline showed that aluminum cresylate gels were less sensitive to the different hydrocarbons than is Napalm Thickener.

4. Exposure tests on aluminum cresylate solutions showed that "skinning" tendency is due to reaction of atmospheric moisture with the cresylate rather than evaporation of the diluent.

5. Use of high boiling diluents for aluminum cresylate was investigated and it was found that refined lubricating oil could be used without excessive loss in consistency of the corresponding gels.

6. Reaction of cresylic acid with various forms of aluminum in the presence of high boiling diluents showed that either granular or foil aluminum can be used satisfactorily in the preparation of aluminum cresylate.

7. Storage tests were made in containers of various materials over a period of three months showed that tin plate, terne plate, iron, and glass were suitable as containers for aluminum cresylate solutions.

8. A satisfactory procedure for the manufacture of aluminum cresylate was developed in pilot scale equipment which could be readily adapted to commercial practice.

9. Relationships were established between consistency and aluminum cresylate concentration, together with the effect of varying the aluminum cresylate-oleic acid ratio, on gasoline gels prepared with these materials.

10. Comparison of 2/3 reacted and 100% reacted products in refined lubricating oil showed that the 100% reacted material was too viscous for handling in the field unless some polar compound was added. However, these polar compounds were found to be excellent peptizers for the gasoline gels, resulting in low consistency.

11. In view of the minor differences in inflammability of the 2/3 and 100% reacted aluminum cresylates, it was considered that the 2/3 reacted product was satisfactory on the basis of meeting Navy's requirements.

12. It was found that moisture is essential for the interaction of aluminum cresylate and oleic acid in the preparation of gasoline gels. The introduction of this moisture is best accomplished by adding a water-acetone blend to the oleic acid used in formation of the gasoline gels.

13. A formulation was developed for the preparation of gasoline gels by "in situ" formation of aluminum soap through reaction of an aluminum cresylate solution in lubricating oil with an oleic acid-acetone-water blend. This adopted formulation gave the gel consistency desired by the Navy for fire bomb mixes.

INTRODUCTION

During World War II thickened fuels were developed for incendiary bombs and flame throwers, the most commonly used product being Napalm Thickener which is a basic aluminum soap of oleic naphthenic, and cocoanut fatty acids. In the latter months of the war in the Pacific, the Navy used fire bombs directly from carriers in order to eliminate enemy concentrations at invasion points. These bombs consisted of "jettison" fuel tanks into which a mixture of gasoline and finely ground Napalm Thickener was introduced by means of special mixing devices. Considerable difficulty was encountered in obtaining uniform mixing, resulting in stratification and incomplete gelation. To eliminate this difficulty, consideration was given to the use of special materials which would give the required gelation by "in situ" formation of aluminum soaps in the gasoline. A number of products had already been investigated by Dr. Alexander of Cambridge University, the more promising of which was aluminum cresylate. His research work had shown that coal tar cresylic acids could be made to react with metallic aluminum to produce aluminum cresylate. On dissolving the aluminum cresylate in an equal weight of benzol, a fluid product was obtained. This solution, when poured into gasoline containing oleic acid, gave good gels. As a result of this work, the English Petroleum Warfare Department developed Camgel XQ Fuel to take the place of F.R.A.S. fuel. The aluminum cresylate component was prepared by reacting cresylic acid, having a high ortho-cresol content, with aluminum foil in the presence of a mixture of coal tar solvent naphtha and coal tar heavy naphtha. The fatty acid solution, commonly used in reacting with the aluminum cresylate, was made up of a mixture of oleic acid, cresol, water, and acetone. Preparation of fuels from these two components was accomplished by first dissolving the aluminum cresylate solution in gasoline and then adding the fatty acid solution while stirring. When a slight thickening occurred this mixture was transferred to the flame thrower tanks and completion of gelation was allowed to take place in the fuel container.

In adapting such a product to our own requirements, it was necessary first to investigate the availability of raw materials. Since coal tar cresylic acid of the particular quality used by the English was not available in the quantity required, consideration was then given to the possibility of using petroleum derived cresylic acids which were available. The first experiments followed closely those of Dr. Alexander and were made for purposes of evaluating the various grades of petroleum acids in comparison with blends of the isomeric cresols.

Experimental work was also done on the effect of gasoline composition since the Navy would use 100 octane gasoline in its mixes for fire bombs. The composition of 100 octane gasoline may vary considerably depending on its source, being only one or a blend of natural gasoline, aromatics, alkylate and catalytic cracked stocks. Comparative tests were made with regular S-130 aviation gasoline to determine if any marked differences in gel character or consistency would be encountered if the gasoline had a preponderance of any one of the above components.

Since the Navy requirements for such agents would necessitate storing in drums on aircraft carriers, the Navy further stipulated that these components should be relatively non-inflammable in order to avoid excessive fire hazards in the event of fire aboard the carrier. Since even heavy coal tar naphtha is considered inflammable, it was necessary to investigate the possibility of using diluents such as lubricating oils to determine if they could be used without adverse effect on either the base stock or the jellied gasoline. Comparative tests were made on both refined lubricating oil and corresponding petroleum distillates.

Consideration of commercial manufacture of aluminum cresylate solutions required pilot scale experimental work for the development of a suitable formulation and production technique adaptable to large scale operation. Pilot plant batches were prepared in accordance with the procedure considered most satisfactory from laboratory experience.

CHAPTER I

PREPARATION OF ALUMINUM CRESYLATE

A. Coal Tar vs. Petroleum Derived Aluminum Cresylates

In the evaluation of petroleum cresylic acids as raw materials for preparation of aluminum cresylate, it was considered necessary to establish standards by which the products could be appraised. Since all previous work has been with coal tar acids, samples of aluminum cresylate were first prepared with high purity cresols. Following are the blends used in preparation of these aluminum cresylates:

(1) Meta-cresol
(2) 50% meta, 50% para-cresols
(3) 60% ortho, 20% meta, 20% para-cresols.

The method used for these preparations was that of Dr. Alexander's in which two-thirds of the theoretical amount of aluminum was utilized, based on the following equation:

$$Al + 3\,\phi\,.CH_3\,.OH \xrightarrow[\text{Heat}]{I_2} Al\,(\phi.CH_3.\phi)_3 + 1\,1/2\,H_2 \uparrow$$

This was accomplished by placing the cresol in a round bottom flask and immersing in an oil bath maintained between 350-360°F. (CA 180°C.). After the stock had reached bath temperature and had been dehydrated, one-third of the aluminum in the form of foil and a small amount of iodine were added. The flask was then connected to a reflux condenser. After several moments, a somewhat vigorous reaction took place. The bath was then allowed to cool to between 320-330°F. and, after the first increment of aluminum was dissolved, the balance was added and the mixture held at the lower temperature. When the reaction slowed considerably, additional iodine was added and heating was continued until reaction was complete. The product was cooled and then dissolved in sufficient benzene to make a 50% solution.

These aluminum cresylates were then tested by mixing with the following blend:

100 parts gasoline (CWS 196-131-144A)
3 parts oleic acid
1 part meta-cresol

To determine the effect of concentration upon consistency, gels were made using 5, 4, and 3 parts of cresylate. The mixture was agitated vigorously with an air stirrer for 4-5 minutes and then transferred to storage tubes. Consistencies were taken at 77°F. with a Gardner mobilometer at one, four, and twenty-four hour intervals.

The petroleum cresylic acids were treated and evaluated in the same manner as used for the cresols, the formulas being modified only to correct for molecular weight. The two grades used were identified as purified "EE" and purified "FF." Their physical and chemical properties are shown in the appendix.

The results of the above experiments were as follows:

Table I

Phenol Used	Concentration % by Vol.	Mobilometer Test - Grams*		
		1 hr.	4 hrs.	24 hrs.
m-Cresol	5	243	218	218
	4	142	147	108
	3	54	36	0
m,p-Cresol	5	156	176	212
50% meta	4	122	140	168
50% para	3	66	72	0
o,m,p-Cresol	5	253	290	271
60% ortho	4	132	145	158
20% meta	3	68	50	0
20% para				
Petroleum Cresylic Acids				
Purified "EE" grade	5	212	241	301
	4	165	218	128
	3	60	76	30
Purified "FF" grade	5	191	268	270
	4	148	170	203
	3	60	80	52

*Note: Regular Gardiner mobilometer readings - grams/10 cm. fall /100 secs.

It can be seen that the gels derived from the ortho-meta-para blend appear the best of the cresol mixes. Those obtained from the petroleum cresylic acids, although in general similar, are somewhat less effected by aging. It would seem, from the limited tests performed, that these latter acids produce aluminum cresylates slightly superior to those derived from the cresol blends.

B. Concentration - Consistency Relationship

Since the Navy desired consistencies in the order of 200-500 grams (Gardiner mobilometer) additional tests were made with higher concentrations of the two petroleum derived aluminum cresylates evaluated above, in order to determine the ranges of concentration which would comply with this requirement. These were prepared with six and seven per cent of cresylate (50% solution) and proportional increases in the oleic acid used. In these tests, the procedure was somewhat modified in that the cresylate was first dissolved in the gasoline and the oleic acid was added to this mixture while agitating. The results of these experiments were as follows:

Table II

Cresylate Acid Used	Concentration % by Vol.	Mobilometer Test - Grams		
		1 hr.	4 hrs.	24 hrs.
Purified "EE" grade	6	355	405	402
	7	420	512	518
Purified "FF" grade	6	335	425	465
	7	365	465	568

These results show that consistency vs. concentration is essentially a straight line function and that the final consistency is dependent on both concentration and time between mixing and utilization.

C. Effect of Cresylic Acid Quality on Aluminum Cresylate

The cresylic acids used above were stocks which had been treated for removal of contaminating sulfur compounds and were not representative of commercial production. To determine if the presence of contaminants (sulfur or neutral oil) or higher boiling phenols was detrimental, additional samples of cresylates were compared from cresylic acids which had not been treated for removal of sulfur. These acids are identified as regular "E" and heavy "FF" grades and their properties are shown in the appendix. The gels of the corresponding cresylates had the following consistencies:

Table III

Cresylic Acid	% (by Vol.)	Mobilometer Tests		
		1 hr.	4 hrs.	24 hrs.
Regular "E" grade	6	220	295	220
	8	388	418	428
Heavy "FF" grade	6	←	No gel	→
	8	205	210	235

From these results it can be concluded that the presence of contaminating materials results in a reduction in consistency. However, it appears that the more important property of the cresylic acid to be considered is its boiling range. Since the heavy "FF" grade cresylic acid is composed of xylenols and higher homologs, it differs considerably from the purified "FF" grade used in the earlier experiments.

On the basis of the results obtained in these tests it was considered that future evaluations of petroleum cresylic acids in the preparation of aluminum cresylate would be made using regular "E" grade.

D. Effect of Gasoline Quality on Aluminum Cresylate Gels

In the preparation of aluminum cresylate gels under field conditions, especially Navy's use in preparation of fire bombs, it is highly probable that the gasoline used would be aviation grade. To determine what effect variations in composition of the gasoline would have on the corresponding gel, a series of tests was made with the following stocks to determine if gel consistency was affected by the type of gasoline used:

1. HF Alkylate (from mixed butenes and pentenes)
2. Isopentane
3. "Thermofor" catalytic cracked (Bead catalyst in primary and retreat units)
4. 100-octane gasoline blend (S-130)

Physical and chemical properties of these gasolines are shown in the appendix. Six per cent aluminum cresylate gels were prepared in the usual manner in the above gasolines. The mobilometer tests obtained on these gels were as follows:

Table IV

Gasoline	Mobilometer Consistencies 1 hr.	4 hrs.	24 hrs.
HF Alkylate	315	346	368
Isopentane	305	350	450
TCC Aviation	318	360	370
S-130	310	400	430

From the results of these experiments, it can be concluded that no marked difference in gel consistency may be anticipated when using various gasolines. In addition they show that aniline point need not be considered as a factor in gel consistency as is the case with Napalm Thickener.

E. Consistency vs. Aluminum Cresylate-Oleic Acid Ratio

Since the English work had indicated that the characteristics of gels were dependent on the ratio of oleic acid to aluminum cresylate, a series of gels was made using six per cent aluminum cresylate in S-130 grade gasoline, varying the amount of oleic acid added for gelation. Following are the results obtained on these tests:

Table V

% Oleic Acid (by Vol.)	Mobilometer Tests 1 hr.	4 hrs.	24 hrs.
2.4	325	300	265
3.6 (standard amt.)	305	360	392
4.8	268	318	305

These mobilometer tests show that the use of the lesser amount of oleic acid gave a gel which was very short and tended to be unstable, making it difficult to obtain reproducible mobilometer readings. The excess oleic acid produced a "stringy" gel similar in appearance to the one in which the standard amount of acid was used. Its consistency, however, was somewhat lower due to the peptizing effect of the increased fatty acid content.

F. "Skinning" Tendency of Aluminum Cresylate Solutions

Experience with aluminum cresylate-benzene solutions has shown that such materials tend to skin on exposure. In order to determine if this skinning was due to evaporation of the benzene or moisture pick-up from the atmosphere, a series of tests was made in which the product was exposed under various humidity conditions. This test consisted of adding a measured volume (20 cc.) of the cresylate solution to an open dish 5 cm. in diameter. Avoiding any drafts, this sample was exposed to the atmosphere and the length of time recorded for the surface to skin completely. Relative humidity determinations were made at the start and finish of the experiment. The following data were obtained:

Table VI

	Temperature, °F.			Skinning Time,
Test	Dry Bulb	Wet Bulb	Relative Humidity, %	Min.
1	78	71	71	2
2	77	69	67	2-1/2
3	82	73	65	2-1/2
4	77	62	42	3-1/2
5	76	61	41	3-1/2
6	75	60	39	3
7	79	59	28	22

With a relative humidity of 30% or less the stock appears fairly stable. However, under conditions of higher humidity, skinning is greatly accelerated. It can be concluded from these results that skinning is due to absorption of atmospheric moisture rather than evaporation of the benzene used as a diluent.

CHAPTER II

ALUMINUM CRESYLATE IN HIGH BOILING DILUENTS

A. Comparison of Various Diluents for Aluminum Cresylate

Preparation of aluminum cresylate solutions meeting Navy requirements of minimum inflammability was considered on the basis of substituting high boiling or non-inflammable diluents for the benzene and coal tar solvents used by the English. Lubricating oil, having a high flash point, was considered as the most readily obtainable diluent meeting these requirements. Another possibility was the substitution of non-inflammable organic solvents such as carbon tetrachloride.

In order to correlate consistency with the type of diluents used, the aluminum cresylates were prepared in accordance with Dr. Alexander's procedure which consisted in dissolving two-thirds of the theoretical aluminum in regular "E" grade cresylic acid at a temperature of 330-360°F., adding sufficient iodine to catalyze the reaction. When the reaction was complete sufficient diluent was added to obtain a solution having 0.6 gram of aluminum cresylate-cresylic acid per cubic centimeter.

Three cresylate solutions were made by the above procedure using benzene, carbon tetrachloride, and a highly refined lubricating oil as solvents. Gels were prepared with these three materials, adding five parts of the cresylate solution and one part meta-cresol to S-130 grade gasoline with the subsequent addition of three parts of oleic acid. Gelation was obtained with both the benzene and lubricating oil stocks; however, the carbon tetrachloride solution remained fluid. In view of these results it was considered possible that less highly refined lubricating oils or high boiling aromatic hydrocarbons might be equally satisfactory, and two additional aluminum cresylate solutions were prepared with lubricating oil distillate and a synthetic aromatic oil as solvents. These cresylate solutions were also used in the preparation of gasoline gels in the above manner. The mobilometer tests on these four stocks were as follows:

Table VII

Solvent Used	Mobilometer Test 1 hr.	4 hrs.	24 hrs.
Benzene	205	228	238
Highly refined lubricating oil	263	265	268
Lubricating oil distillate	160	184	168
Synthetic aromatic oil	177	195	148

It will be noted that the product in highly refined lubricating oil gave gels with the highest consistencies. This indicates that the presence of aromatics and unsaturates in the diluent results in a material reduction in consistency. For purposes of comparison, physical properties of these three high boiling stocks are shown in the appendix.

In the above preparations, the normal procedure has been first to complete the reaction of cresylic acids with aluminum at a temperature of 360°F., adding the diluent after evolution of hydrogen has ceased. Since the English experience showed that a diluent could be added to the cresylic acids prior to reaction with aluminum, permitting the use of lower temperatures and allowing the reaction to proceed uniformly, an experiment was made following this procedure while maintaining the stock at a temperature of 300°F. The reaction began shortly after addition of the iodine catalyst and continued very smoothly until completed. The elapsed time for this reaction was less than that previously required when no diluent was used and higher temperatures employed.

B. Reactivity of Various Forms of Aluminum

Using the above procedure, a series of experiments was made in which various forms of aluminum were used, as follows:

1. Thin foil (.0025" thick)
2. Thick foil (.0048" thick)
3. Granular (16 mesh and finer)
4. Wire (0.078" diam.)

The reaction in each case starting shortly after the addition of the iodine and proceeding through to completion satisfactorily. The granular aluminum was dissolved in the shortest length of time. The two foils behaved similarly, taking only a slightly longer time for reaction. The aluminum wire, which offered the least reactive surface, required considerably longer time for completion of the reaction. From these results it can be concluded that granular aluminum is entirely satisfactory and, because of its form, lends itself to handling readily in preparation of aluminum cresylate.

C. Pilot Scale Preparation of Aluminum Cresylate

The english Camgel base stock has been prepared in a more concentrated form than the materials indicated in previous experiments, containing 0.7 grams per cubic centimeter of aluminum cresylate. To determine if a similar concentration could be obtained when lubricating oil was substituted for the coal tar solvent, a pilot batch was prepared in a Pfaudler kettle, equipped with a full steam jacket and mechanical agitator. Following is the batch formula for this preparation:

Regular "E" grade cresylic acid	124 lbs.
Aluminum (granular)	6.6 lbs.
Highly refined lubricating oil	56.4 lbs.
Iodine	2.0 lbs.

The cresylic acid and lubricating oil were charged to the kettle, and the temperature raised to 310°F. while agitated. Vacuum was applied to the kettle for thirty minutes to eliminate moisture from the mixture. The vacuum was then released and the aluminum and iodine added in increments of 1.65 lbs. and 0.5 lb., respectively. On addition of the first increment of these two materials, the temperature of the batch rose to about 360°F. at which point cooling water was added to the jacket at such a rate that the temperature of the batch was held below 370°F.

When evolution of hydrogen ceased, the second increment of aluminum and iodine was added and the same procedure followed. These additions were repeated until all stock had been added and the mixture maintained at the temperature in excess of 300°F. for 30 minutes after cessation of hydrogen evolution. The stock was then cooled to 200°F. and filled directly into containers for storage.

D. Containers for Aluminum Cresylate Solutions

Since information was lacking on the effect of type of container required for aluminum cresylate, samples were filled into tin plate, terne plate, iron, and glass containers. These containers were placed in storage for tests after three months. After this storage period, mobilometer tests were made for comparison with the original results of tests made at the time of preparation of the aluminum cresylate. Following are the results of these tests together with the original consistency values:

Table VIII

Container	% by Vol.	Mobilometer Test 1 hr.	 4 hrs.	 24 hrs.
tin plate	5	350	410	360
terne plate	5	340	400	355
iron	5	247	380	495
glass	5	220	250	285
Original tests	5	418	430	445

Although these tests would indicate that the type of container may affect the aluminum cresylate, it is believed that these differences are not significant but represent the usual experimental variations.

E. Effect of Varying Quantities of Cresol and Oleic Acid on Gel Consistency

More complete tests were made on the use of this particular aluminum cresylate in the preparation of gel varying the amount of cresol and oleic acid used in the jellying experiments. Tests were also made following the "Camgel" procedure. Following are the results obtained in these experiments:

Table IX

% Aluminum Cresylate	% Cresol	% Oleic Acid	% Water	% Acetone	Mobilometer Tests 1 hr.	 4 hrs.	 24 hrs.
5	1	5	-	-	418	430	445
5	1	7	-	-	405	398	215
4	1	4	-	-	273	325	158
5	2	5	-	-	405	418	228
5	3	5	-	-	233	203	60
5.5*	1	6.1	0.08	0.8	300	175	15

*Note: Made in accordance with "Camgel" procedure.

These tests show that the use of equal volume of the cresylate and oleic acid will give the maximum consistency. The addition of a greater amount of oleic acid reduces consistency due to the peptizing action of the unreacted fatty acid. Increasing the amount of cresol added serves only to peptize the gel further and is probably not required since the original cresylate contains free cresylic acids in a quantity sufficient to give the desired peptization. The low consistencies obtained with the "Camgel" mixture are due to the combined effect of the larger amount of oleic acid and the water resulting in excessive peptizing of the gel.

F. Use of Moderately Refined Lubricating Oil as a Diluent

The use of less highly refined lubricating oils was considered since the available supply of oils such as that used in previous experiments is limited. To determine if moderately refined oil could be used without adverse effect on the property of the aluminum cresylate, a pilot batch was prepared in accordance with the same procedure used in the previous experiment. Gels were prepared from this material by adding cresylate solution to S-130 grade 100 octane gasoline, followed by the addition of an equal amount of oleic acid. Mobilometer tests on the resulting gels gave the following consistencies:

Table X

	Mobilometer Tests		
% by Volume	1 hr.	4 hrs.	24 hrs.
5	315	348	213
6	435	510	390
7	510	668	600

Comparison of these results with those obtained when using the aluminum cresylate in highly refined lubricating oil shows that the degree of refinement is reflected in the performance of the aluminum cresylate. However, the difference between these two stocks is a matter of degree, since both stocks comply with Navy requirements at the same concentration.

G. Effect of Free Cresylic Acid on Inflammability of Aluminum Cresylate Solutions

As a high flash cresylate solution is required by the Navy, it was considered that the presence of the one-third unreacted cresylic acid might be undesirable because of its effect on the flash point. A laboratory batch of cresylate was prepared using the same ingredients as the pilot batch run except that sufficient aluminum was added to react with all of the cresylic acids to give a 100% reacted product. This cresylate was very viscous and difficult to handle for mixing operation. Gels prepared from this material gave the following consistency measurements:

Table XI

	Mobilometer Test		
% by Vol.	1 hr.	4 hrs.	24 hrs.
5	350	438	470

Comparison of results obtained on the two-third reaction and the 100% reaction products shows that the degree of improvement in consistency is not in the same order which would be expected on the basis of actual aluminum cresylate content.

To determine if the addition of more diluent would reduce the viscosity without excessive loss in consistency of the gasoline gel, two portions of the 100% reaction product were diluted with 1/4 volume of the same refined lubricating oil and 1/4 volume of carbon tetrachloride. The addition of the lubricating oil had only a slight effect in reducing viscosity; however, the product of which the carbon tetrachloride had been added was a fluid product. Gels prepared from these two diluted products had the following consistencies:

Table XII

Modified Cresylate	% by Vol.	Mobilometer Test 1 hr.	4 hrs.	24 hrs.
CCl_4 added	5	120	155	115
Lub. oil added	5	102	114	58

These results show that the lubricating oil is an excellent peptizer in its own right being even more effective than free cresylic acid. The use of smaller amounts of carbon tetrachloride might result in a product of satisfactory fluidity without a great loss in gel consistency. In view of the result obtained on gels prepared with the 100% reacted product, it was considered that the basis of comparison of this material with the two-thirds reacted product should be their inflammabilities as indicated by flash points and fire points. Following are the tests on these two products:

	2/3 Reacted	100% Reacted
Flash Point Cleveland, °F.	260	290
Fire Point, °F.	290	320

Although these results indicate a slight improvement in the 100% reacting product the reduction in inflammability is insignificant as far as eliminating a potential hazard in the event of fire aboard the carrier.

Before discontinuing work along the lines of raising the flash point small batches of cresylate were prepared in a heavy lubricating oil (bright stock of 185 vis. SSU at 210°F.), corresponding to the 2/3 reacted and 100% reacted products. Both products were excessively viscous and formed inferior gels of lower consistencies.

H. Use of Polar Compounds in Aluminum Cresylate Solutions

Another possible means of producing a low viscosity material which would flow readily at normal temperature and yet have a high flash point, was the use of a synthetic high molecular weight alkyl phenol in place of the free cresylic acid normally present in the two-third reacted product. Two experimental batches of cresylate were made using an alkyl phenol having properties shown in the appendix. The first product was prepared as a 100% reaction cresylate and while still hot a quantity of the alkyl phenol was added equal to half of the original cresylic acid volume. The second preparation, involving the same components, differed in that the high boiling phenol was added at the start of the reaction. The flash and fire points of these stocks were as follows:

	Added at Start	Added at Finish
Fire Point Cleveland, °F.	285	295
Fire Point, °F.	300	310

From these results it can be concluded that some improvement is obtained by a substitution of the free cresylic acid with the heavy alkyl phenol. However, here again the difference is not of significance as far as eliminating potential fire hazard.

For comparison of these products with the normal formulations gel consistencies were obtained on the two products at different concentrations. Results of these tests were as follows:

Table XIII

	% by Vol.	Mobilometer Tests		
		1 hr.	4 hrs.	24 hrs.
Added at Start	(5	68	99	192
	(6	101	131	260
	(7	205	318	314
Added at finish	(5	68	95	220
	(6	163	330	365
	(7	216	400	480

These tests show that the heavy alkyl phenol has somewhat greater peptizing properties than the regular cresylic acid and there is some indication that these materials tend to delay gelation. However, in comparison with the results obtained on the normal two-thirds reacted product, these products appear to retain consistency between four hours and twenty-four hours.

As a result of our findings in this preliminary work, it was concluded that the principal differences in the English "Camgel" material and our product in lubricating oil were due to the inferior solvent power of lubricating oil as compared with low boiling aromatic hydrocarbons. Thus it is necessary to have some polar compound such as the cresylic acids present in order to obtain comparable viscosities. From the limited work on the use of other polar materials it was considered possible that some chlorinated hydrocarbon of lower volatility than carbon tetrachloride might be used to reduce viscosity and maintain a high flash point.

CHAPTER III

FINAL FORMULATION FOR ALUMINUM CRESYLATE SOLUTION

A. Effect of Moisture on Gel Formation

On the basis of our findings as indicated in Chapter II, all efforts towards the development of a final formula were concentrated on aluminum cresylate prepared as a two-third reacted product in refined lubricating oil. The other variables which were considered important were the effect of moisture and the oleic acid-aluminum cresylate ratio used in the preparation of gels.

Heretofore in the experimental preparation of gels with the aluminum cresylate, mixing had been done in open vessels in such a manner that the surface was exposed to the atmosphere during the period of mixing. Since the Navy procedure of mixing would probably be in a closed system, tests were made in which an inert atmosphere of nitrogen was maintained over the surface during the mixing. Gels obtained from these experiments were low in consistency as compared with the same formulation mixed in the open. This indicated that moisture was being taken up during the mixing, accelerating gelation. In reviewing the English work it was considered possible that comparable results could be obtained in a closed system if the necessary moisture could be added with the oleic acid as an acetone-water mixture. A series of tests was made in this manner using six per cent of the two-thirds reacted aluminum cresylate in refined lubricating oil and a corresponding amount of oleic acid to which had been added various quantities of the acetone-water blend. Results of these tests, together with that of the blank are shown in the following table:

Table XIV

% Aluminum Cresylate	% Oleic Acid	% Acetone	% Water	Mobilometer Tests		
				1 hr.	4 hrs.	24 hrs.
6	6	-	-	142	160	below 60
6	6	0.30	0.03	575	610	400
6	6	0.45	0.045	600	525	365
6	6	0.60	0.06	405	305	292

These tests are definite proof that moisture is essential for the reaction to take place. Comparing these results with those obtained in the open mixing experiment, it will be noted that the variations obtained in the latter tests are within the range of the consistency shown in the above table for those stocks to which acetone-water was added, indicating that absorption of moisture from the atmosphere is dependent on humidity and time of exposure.

B. Effect of Aluminum Cresylate-Oleic Acid Ratio on Gel Consistency

A series of gels was prepared by mixing in the open in which the aluminum cresylate was used in concentration of 5, 6, and 7 per cent. The quantity of oleic acid was varied from 80 to 120% of the aluminum cresylate volume. Consistencies of these gels were as follows:

Table XV

% Aluminum Cresylate	% Oleic Acid	Mobilometer Tests 1 hr.	4 hrs.	24 hrs.
5	4	400	455	360
5	5	363	426	275
5	6	177	210	165
6	4.8	585	570	330
6	6.0	480	535	352
6	7.2	310	355	205
7	5.6	650	800	585
7	7	890	945	985
7	8.4	425	400	255

It will be noted that the most uniform gels are obtained when the ratio of oleic acid to aluminum cresylate is 1:1, the use of more oleic acid tending only to peptize the gel further. This difference is even more marked where a higher concentration of aluminum cresylate solution is used.

C. Final Formulation for Navy Type Gels

On the basis of the above experiments the final formulation of the aluminum cresylate solution considered most satisfactory would be a two-third reacted product in refined lubricating oil prepared in accordance with the procedure given in the appendix for manufacture of a 150-gallon batch.

The oleic acid solution would be made up by adding to each gallon of oleic acid, the following:

Acetone	0.1 gallon
Water	0.01 gallon

Using these two base stocks, 100 gallons of gasoline would be mixed with 6 gallons of the aluminum cresylate solution followed by additional mixing with 6.66 gallons of the oleic acid solution. The mixed stock could then be filled directly into the fire bomb where gelation could continue until the desired consistency of 200 to 500 grams was obtained. From the above table it can be seen that maximum consistency would be obtained in less than an hour after mixing which should be rapid enough for the service required by the Navy.

Fifty gallons of aluminum cresylate solution, prepared in accordance with the above formulation, was shipped September 11, 1945 to Captain John A. Southern at Edgewood Arsenal for use in large-scale field tests in fire bombs.

CHAPTER IV

PITFALLS

1. In the preparation of aluminum cresylate solution, there are several hazards which should be avoided. One of the principal pitfalls is the presence of moisture in the cresylic acid which prevents reaction of the metallic aluminum and the cresylic acid. Our regular practice for removal of water has been to heat the cresylic acid to a temperature in excess of 300°F., applying sufficient vacuum to remove the moisture. The English procedure is to add a small amount of aluminum cresylate from a previous batch to the cresylic acid prior to the addition of the aluminum. Both procedures are satisfactory for the removal of water.

2. Precautions must be taken to insure minimum oxide coating on the metallic aluminum since this prevents its reaction with the cresylic acid. This can be accomplished either by pre-treatment of the aluminum with aqueous solutions of heavy metal salt such as mercuric nitrate - or by the addition of iodine during the reaction.

3. The presence of excessive amounts of polar compounds in either the cresylic acid or the gasoline used in the preparation of the gel will tend to give low consistency.

4. Composition of the cresylic acid used is of importance since high boiling components above xylenol are excellent peptizers and also do not react as readily as a lower boiling phenol.

APPENDIX I

Batch Formula

Cresylic acid (regular "E" grade)	100 gallons
Refined lubricating oil	53 gallons
Aluminum (granular)	48 pounds
Iodine crystals	12 pounds

Equipment

Steam and water jacketed kettle with mechanical agitation and equipped with necessary appurtenances for application of vacuum, removal of reaction gases, reagent injection, and equipment for filling stock into containers.

Procedure

Charge the cresylic acids and refined lubricating oil to the kettle and heat to 300-310°F. temperature. Apply vacuum gradually until pressure is reduced to 5 inches mercury. Maintain under these conditions for 30 minutes to insure elimination of water. Release vacuum and raise temperature to 320-330°F. Add 12 pounds of aluminum and 3 pounds of iodine while agitating. Observe closely the temperature of the mixture and when it reaches 360°F., inject water into the jacket at such a rate to maintain the temperature between 360 and 370°F. When evolution of hydrogen subsides, repeat the cycle of adding aluminum and iodine until all four increments have been added. The mixture is maintained above 300°F. for 30 minutes after hydrogen evolution has ceased then cooled to 200°F. and loaded into the desired containers.

APPENDIX II

PROPERTIES OF NEUTRAL OIL DILUENTS

	Highly Refined Lubricating Oil	Lubricating Oil Distillate	Refined Lubricating Oil	Synthetic Aromatic Oil	Bright Stock
Flash Point, °F. (Clev.)	350	320	350	270	595
Fire Point, °F.	375	-	385	300	665
Vis. at 100°F., SSU	78.7	105	103.9	48.5	4180
Pour Point, °F.	-15	-40	-	-50	-
Aniline Point, °F.	205	119	151	-	-
% Unsulfonated Residue	100	57	98.0	nil	-
Distillation, ASTM	D-158	D-158	D-158	D-158	at 1.5 mm. Hg.
Start	580°F.	530°F.	593°F.	483°F.	520
5%	620	570	618	511	-
10%	624	590	624	519	583
20%	630	609	637	529	595
30%	637	625	646	541	615
40%	642	640	653	555	632
50%	648	654	661	575	-
60%	658	668	669	596	-
70%	672	692	680	626	-
80%	690	716	695	669	-
90%	720	736	719	740	-

APPENDIX III

PROPERTIES OF GASOLINES

	S-130	HF Alkylate	Isopentane	Thermofor CC
Aniline Point, °F.	120	167.2	173	68
Bromine Number	-	.12	.77	-
Hydrocarbon Distribution -				
% Olefins	1	0.05	0.3	1
% Aromatics	11	0.32	0.0	35
% Paraffins	68	99.6	99.7	41
% Naphthenes	20	0.0	0.0	21
ASTM Distillation				
Start	104°F.	148°F.	81°F.	103°F.
5%	138	188	82	125
10%	150	197	83	134
20%	169	210	83	146
30%	186	217	83	162
40%	202	223	83	183
50%	218	228	83	210
60%	230	233	83	236
70%	240	239	83	257
80%	254	249	84	272
90%	278	275	85	283
95%	296	323	87	291
End Point	342	356	128	301

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APPENDIX IV

PROPERTIES OF PHENOLS

	Purified "EE"	Purified "FF"	Regular "E"	Heavy "FF"	Heavy Alkyl Phenol
Specific Gravity at 60°F.	1.028	1.007	1.022	1.005	-
% Neutral Oil	0.05	0.1	0.5	0.4	-
% Water (by distillation)	0.2	0.5	0.3	0.2	-
% Sulfur (Bomb)	0.12	0.1	0.42	0.22	-
Distillation-ASTM	D-86(Mod)	D-447	D-447	D-447	14 mm. Hg.
Start	395°F.	420°F.	390°F.	426°F.	294°F.
5%	397	426	402	438	314
10%	399	430	404	440	332
20%	400	432	405	441	347
30%	401	435	-		372
40%	403	436	-		391
50%	406	437	409	444	406
60%	408	439	-		414
70%	410	441	-		428
80%	412	443	-		450
90%	416	448	419	452	508
95%	424	454	423	456	
End Point	443	463	448	476	

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Tests were conducted to determine if petroleum cresylic acids were suitable for the manufacture of aluminum cresylate used for "in situ" formation of gasoline gels in incendiary bombs and flame-throwers. Gel preparations with various types of aviation gasoline showed that aluminum cresylate gels were less sensitive to the different hydrocarbons than Napalm Thickener. Exposure tests on aluminum cresylate solutions showed that "skinning" tendency is due to reaction of atmospheric moisture with the cresylate, rather than to evaporation of the diluent. A formulation was developed for the preparation of gasoline gels by "in situ" formation of aluminum soap through reaction of an aluminum cresylate solution in lubricating oil with an oleic acid-acetone-water blend. This adopted formulation gave the gel consistency desired by the Navy for fire bomb mixes.

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23 * Incendiary Bombs,
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25 Incendiary Applications
Gasolene Gels