ENCLOSURE (B)26

PART II

MANUFACTURE OF LUBRICATING GREASE FROM SYNTHETIC LUBRICATING OIL IN PLACE OF NATURAL OIL

by

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SUMMARY

In studying various synthetic lubricating oils as base oils for the manufacture of various greases, it was observed that for the calcium or sodium soap greases, condensation products of olefinic and aromatic hydrocarbons were suitable.

I. INTRODUCTION

When soaps are mixed in mineral oil with agitation and this mixture is heated, gradually the soap dissolves in the mineral oil. On cooling, dissolved soaps are crystallized out. The mineral oils as the dispersion medium are enveloped by the crystal structure, and it is assumed that a special structure such as a honey comb form is produced. Then, there are protective colloidal matters to guard the arrangement of this crystal structure. The protective matters in the case of calcium soap are hydroxide compounds such as water, alcohol, glycerine sugars, etc. When synthetic oil was used in place of natural mineral lubricant investigations were made to determine whether paraffinic or aromatic synthetic types of oils were more suitable for the manufacture of greases. Generally the natural lubricant from crude oil consists of aromatic hydrocarbons, which have good solubility and affinity for soaps compared to paraffinic hydrocarbons.

It was concluded that the condensation product of olefinic hydrocarbons and aromatic hydrocarbons (naphthalene, benzene, etc.) would be suitable. Low viscosity oils, in general, have the property of good solubility in soap, so that, even paraffinic polymerization oils of low viscosity would also be suitable to make several types of greases.

These studies were carried on during 1944.

II. DETAILED DESCRIPTION

A. Calcium Soap Base Grease:

In the manufactures of "Cup Grease," containing calcium soaps, two methods are generally used:

1. Calcium soaps (calcium-stearate and oleate) are added to mineral oil, well mixed by stirring and heated to 80°C. Then water (alkaline water solution which contains NaOH below 0.2% for total oil) is added, and heated quickly to 105°C with agitation, until the water content is below 2% as judged by consistency. Then the grease is cooled to 80°C.

2. Fatty acids (stearic-and oleic-acid) are added and dissolved in mineral oil by heating. At below 70°C a slight excess of the theoretical value of calcium hydroxide solution, calculated from the saponification value of the fatty acids, are added. The mixture is heated with agitation, keeping below 105°C, and the excess water is evaporated gradually. When the plasticity increases suddenly, heating is stopped and the temperature is decreased to 80°C.

But in either method, if the calcium soap base grease retains a trace of alkali, it is difficult for the grease to have the desired consistency.

The first method of preparation has the defect that the distribution of water is not uniform, and it is difficult to make grease of uniform composition.

On the contrary, the second method is very easy and provides grease of uniform composition. Generally, the consistency of calcium soap base grease is affected by water content to some extent, the more water, the harder.

B. No. 1 and No. 2 Cup Greases

These greases are mixtures of the calcium soaps and a mineral oil which has a viscosity over 50 Redwood No. 1 sec. at 30°C. and a flash point above 130°C. Natural mineral oil (viscosity about 130 sec. at 30°C in Redwood No. 1 sec.) made from Niizu crude oil, has an aniline point of about 80 and grease of good stability is easily manufactured using this oil.

Polymerization oil made from cracked distilled waxes, which has the same viscosity as the above-mentioned oil, has an aniline point of about 116. In manufacturing the cup grease from the polymerization oil, the soap is mixed in with difficulty and the soap is inclined to separate from the oil. Therefore, with such polymerization oils more than 50% of calcium soap of an unsaturated fatty acid, such as oleic acid, must be added in order to produce good stability grease of higher consistency. However the grease thus obtained does not meet the Naval Specifications in regard to soap content.

When oil prepared by the simultaneous condensation of olefines and aromatic compounds (benzene and naphthalene) is used, a grease can be made which is as stable as natural mineral oil. The synthesis of such oil was carried on as follows: The cracked distillate was polymerized alone or with benzene or naphthalene in the presence of 5% of $AlCl_3$ at 80-100°C for 10 hrs. This product was distilled in a vacuum of 5mm. Hg and the fraction boiling below 300°C. is used as the raw material for making greases. Table XIX(B)36 shows their properties.

Naphthalene-benzene condensation oil, topped to 280°C, has a low aniline point as shown in Table XX(B)36 and is the suitable material for this grease. This method has the advantage of utilizing the by-product (light end) in the synthesis of aero engine oil.

C. Cup Grease for Cold-Proof (low temperature) Grease (so called "No. 4 Grease"

Since the greases of synthetic oil have a lower freezing point than those of natural mineral oil, they should be good for low temperature.

The natural mineral oil (class No. 3 precise oil) had about an 80 aniline point, and so synthetic oils which had aniline points of the same order were prepared from the condensation of the cracked distillate of paraffin wax with benzene, toluene, cyclohexane, naphthalene and benzene, or naphthalene and toluene.

The synthetic oils had pour points below (-) 60°C., so it was possible to prepare good cold proof greases from them. It was found that naphthalene and benzene, and, naphthalene and toluene condensation oils were the most suitable. In order to obtain the lowest pour point of the naphthalene and benzene condensation oil, it was found that a ratio of 15 parts naphthalene to 85 parts of benzene by volume was required, as shown in Figure 5(B)36.

2% of anhydrous aluminum chloride was added and after the catalyst was completely dissolved by heating at about 80°C, four parts of cracked distillate from waxes (boiling from 150°C to 230°C.) to one part of aromatic compound, were dropped in and kept at a high temperature.

Then the aromatic compounds were completely condensed with the cracked distillate and a 50% yield of oil having a pour point below -60°C, was obtained. (When 1.5% of anhydrous $AlCl_3$ and 0.5% of anhydrous $ZnCl_2$ were used, dechlorination of polymer was very easy.)

The properties of "No. 4 Cup Grease" made from this synthetic oil are shown in Table XXI(B)36

D. "Mobile Grease" for Controllable-Pitch Propellers (Known in Japanese Navy as "No. 5 Grease")

It is necessary that the base oil of this grease have a high viscosity (115 S. U. S. at 210°F). Using polymerization oil cracked distillate or its condensation with naphthalene or naphthalene and benzene, good results were obtained as seen in Table XXII(B)36.

Aluminium stearate, aluminium oleate, lead oleate and glycerine are added to about one third of the synthetic oil to be used, heated to about 130°C, with attendant stirring. After the water present is evaporated and the mixing of the soaps in the oil is complete, the remaining two thirds of the oil are added. Keeping at about 130°C, the mixture is well agitated for 3-5 hours, then the grease is cooled to 80°C.

E. Grease for Rocker Arms. (So called "No. 6 Grease")

The base oil used in this study was a condensation oil of cracked distillate of wax with naphthalene and benzene. Table XXIII(B)36 shows its properties.

Fatty acids were added to about one third of the synthetic oil to be used and the mixture was heated while stirring continuously. After adding approximately 20% water solution which contained the calculated amount of sodium hydroxide at about 40°C, the temperature was gradually raised and the water evaporated. Calcium soaps were added at about 130°C and then cooled to 120°C. Next the residual two thirds of oil and

glycerine were put in and well mixed for 1.5 hours at 120°C and then taken out at 100°C.

In manufacturing this grease, one of the most important factors was that the oil be weakly acid when mixed and when free fatty acids were 0.4-0.5%, good results were obtained. But, when the amounts of free acid were below 0.2%, their stability was not only bad, but their consistency was inclined to increase. Although glycerine was effective in providing heat stability, excess glycerine had a tendency to increase the consistency. Consequently the quantity of glycerine is a very significant factor.

F. Magneto Grease (So-called "No. 7 Grease")

Generally, the manufacturing method for this grease was as follows:

About 20% of sodium soaps of castor oil were added to the mineral oil and mixed at more than 200°C. The properties of the base oil were:

Flash point..... above 170°C
Viscosity in Redwood No.1 sec.. over 200 sec at 30°C
Pour point ..... -30°C.(below)

Mineral oil used was a refined distillate of NIIZU crude oil. of which the properties are as follows:

Viscosity in Redwood No.1 sec..... about 208 at 30°C
Aniline point (°C) 81.5
Flash point (°C) 183
Pour point (°C) .....-47

This grease also contained the sodium soap of sebatic acid which formed from the cracking of some ricinoleic acid.

In another case the mixed sodium and calcium soaps were used and heated to 170°C. Then studies were carried on to determine whether oils of either paraffinic or naphthenic structure were suitable for preparing this grease. This work showed that the polymers of cracked wax distillate were not suitable for preparing magneto grease, because the castor oil soap separated.

Table XXIV(B)36 presents the details of the grease preparation from the condensation oil.

Although this is an excellent cold-proof grease, as the table shows, it will be noticed that some soap separates from the oil at the dropping point. However, the stability is improved if the calcium oleate (1%) and glycerine (0.2%) are added Table XXV(B)36 shows the results:

Thus, when the viscosity of oil is about 200 Redwood No. 1 sec. at 30°C and its aniline point is below 90, the naphthenic oil is excellent as the base oil, but oil with an aniline point above 90, however, is not suitable. Therefore, this method was tried using other soaps. In this study, the synthetic oils, aniline points of which are 90-105, were used with mixed sodium and calcium soaps of fatty acids, (stearic and oleic). The results show that these were suitable materials, as seen in Table XXVI(B)32.

Whether castor oil or other fatty acids are to be used, depends upon the aniline point of the base oil. In the case of using sodium soap, castor oil or fatty acids were generally added in ratio of one third of the mineral oil used, and saponified by adding a 20% solution of the calcu-

lated amount of NaOH at 40-70°C. The water present is gradually evaporated by heating to 130°C. In the case of castor oil, after the oil was heated for 30-60 minutes at 200°C (with agitation), the residual two-thirds of mineral oil was added. After agitation, the grease was drawn at 170°C, and cooled quickly.

In the case of mixed-base soaps prepared from fatty acids, the sodium soap was first added to one third of the oil and the mixture heated to 130°C.

Then the calcium soap and glycerine were added and heated to 150°C after which the remaining oil was added. After heating for 1.5 hours, the grease was cooled quickly.

III. CONCLUSIONS

The methods of A - B for "Cup Grease" manufacture are very satisfactory, and one of the most suitable synthetic lubricants is the condensation oil of olefines with naphthalene and benzene.

For cold-proof grease ("No. 4 Cup Grease"), the best base oil is the one which is made by condensation of cracked wax distillate (boiling from 150°C to 230°C) with naphthalene and benzene.

For "Mobile Grease" (No. 5 Grease), a polymerization product of olefines is unsuitable due to soap separation. It is necessary that the properties of condensed oil be as follows:

Viscosity in S. U. S. at 210°F..... ..125
Aniline point (°C) ..... below 15

For "Rocker Arm Grease" ("No. 6 Grease"), polymerization oil is unsuitable, but condensation oil of naphthenic character is suitable.

For "Magneto Grease" ("No. 7 Grease") using the soap of castor oil, the properties of suitable synthetic oil are as follows:

Viscosity in Redwood No. 1 sec.....about 200
Aniline point (°C) below 90

However, if sodium stearate and sodium oleate are used, the condensation oil which has an aniline point above 90 is suitable.

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Table XIX(B)36
PROPERTIES OF SYNTHETIC OILS

	Materials	Temp(°C)	Time (hr.)	$AlCl_3$ (%)
Polymerization oil of paraffin cracked oil	Cracked distillate of wax	80 - 100	8	5
Condensation oil of paraffin cracked oil and benzene	Fraction boiling from 100°C to 250°C of distillate of wax 80	80 - 100	8	5
Condensation oil of paraffin cracked oil and naphthalene	benzol ..... 20 Fraction boiling from 100°C-250°C of distillate wax ..... 80 naphthalene .. 20	80 - 100	8	5

Viscosity (Redwood 1, sec.)			Aniline point (°C)	Pour point (°C)
10°C	30°C	50°C		
640	785	150	118	-15
527.8	155.8	88.1	65	-25
565.6	200.2	95.4	95.4	-25

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Table XX(B)36
COMPOSITION AND PROPERTIES OF SYNTHETIC GREASES
(NO.1 AND NO. 2 CUP GREASE)

Conditions of synthesis — Materials		Naphthalene and benzene condensation	
Time (hrs) ..... 10 Temperature (°C) ..... 80-120 $AlCl_3$ (%) 5		Cracked distillate boiling from 100°C to 250°C of waxes ..... 80 Naphthalene ..... 10 Benzol 10	
Properties of Product			
Viscosity in Redwood no. 1, sec.	at 30°C	93.8	
	at 50°C	42.6	
Aniline point (°C)		56	
Flash point (°C)		58	
Pour point (°C)		-12	
Acid value		0.1	
Saponification value		0.01	
Evaporation loss at 100°C for 5 hrs. (%)		0.08	
Composition of Grease		Order	
		No. 1	No. 2
Synthetic oil		70	73.1
Calcium stearate		21	22.7
Calcium stearate		9	4.2
Properties of Greases		Order	
		No. 1	No. 2
Dropping point (°C)		120	105
Worked consistency at 250°C *		201	230
Free alkali (%)		0.18	0.14
Water (%)		1.41	1.2
Ash (%)		3.0	2.8
Stability		O.K	O.K
Corrosion		O.K	O.K

* Work penetration, A.S.T.M.

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Table XXI(B)36
COMPOSITION AND PROPERTIES OF SYNTHETIC GREASES
(NO. 4 CUP GREASE)

Properties of Materials		Naphthalene and benzene condensation (A)	Naphthalene condensation (B)
Conditions of Synthesis*	Materials	Cracked distillate boiling from 100°C to 250°C of waxes ..... 80 Naphthalene ... 10 Benzene 10	Cracked distillate boiling from 100°C to 250°C of waxes ..... 85 Naphthalene ... 15
Properties of Product			
Vis. in S.U.S. at 210°F		110.0	150
Viscosity index		110.0	113.1
Specific gravity D_4^{20}		0.8539	0.8856
Aniline point (°C)		107.5	109.0
Pour point (°C)		-30	-30
Saponification value		0.16	0.10
Acid value		0.02	0.02
Composition of Grease		(A)	(B)
Synthetic oil		89	89
Aluminium stearate		7.6	7.6
Aluminium oleate		1.2	1.2
Lead oleate		1.2	1.2
Glycerin		1	1
Properties of Grease		(A)	(B)
Appearance		Fibroid, viscous semi-fluid	Fibroid, viscous semi-fluid
Dropping point (°C)		64	68
Worked consistency at 10°C		374	362
Free alkali (%)		-	0.16
Free fatty acid (%)		0.22	-
Corrosion		None	None
Stability		0.5	0.5
Ash (%)		0.73	0.81

* For both condensations, time was 10 hr., temperature was 60°C, and 5% of $AlCl_3$ was used

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Table XXII(B)36
COMPOSITION AND PROPERTIES
(CONTROLLABLE PITCH PROPELLER)

Conditions of Synthesis*	Materials	Naphthalene and toluene condensation (A)	Naphthalene and benzene condensation (B)
		Cracked distillate boiling from 150°C to 230°C of waxes ..... 80 Naphthalene ..... 3 Toluene 17	Cracked distillate boiling from 150°C to 230°C of waxes ..... 80 Naphthalene ..... 3 Benzene 17
	Catalyst	$AlCl_3$: 1.5% $ZnCl_2$: 0.5%	$AlCl_3$: 1.5% $ZnCl_2$: 0.5%
Properties of Products			
Viscosity in Redwood no. 1, secs. at 30°C		168	132.4
at 50°C		70	64
Aniline point (°C)		69	93
Flash point (°C)		162	154
Pour point (°C)		-60	-63
Composition of Greases			
		(A)	(B)
Synthetic oil (%)		82.4	82
Calcium stearate (%)		8.8	9
Calcium oleate (%)		8.8	9
Properties of Greases		(A)	(B)
Dropping point (°C)		101.5	107
Worked consistency	at 25°C	270	269
	at 5°C	220	225 (at 0°C)
	at 25°C	210	210 (at 20°C)
	at 40°C	188	186
Solidifying point (°C)		-43	-40
Free alkali (%)		0.17	0.57
Water (%)		1.8	0.36
Ash (%)		1.6	1.78
Stability		O.K.	O.K.
Corrosion		O.K.	O.K.

*For both condensations, time was 6 hrs, temperature was 80-120°C

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Table XXIII(B)36
COMPOSITION AND PROPERTIES
(ROCKER AND GREASE)

Properties of Materials		Naphthalene and benzene condensation
Conditions of Synthesis*	Materials $AlCl_3$ (%) ..... 5 Temp (°C) ..... 80-30 Time (hrs) 6	Cracked distillate of wax .... 80 Naphthalene ..... 3 Benzene 17
Viscosity in S.U.S. at 210°F		110
Viscosity index		109
Aniline point (°C)		100
Flash point (°C)		220
Pour point (°C)		-38
Acid value		0.03
Saponification value		0.11
Composition of Grease		
Synthetic oil (%)		91.11
Calcium stearate (%)		1.82
Calcium oleate (%)		1.82
Sodium stearate (%)		2.00
Sodium oleate (%)		2.00
Glycerin (%)		1.25
Properties of Grease		
Appearance		fluorescent, semi-fluid smooth texture
Dropping point (°C)		92
Worked consistency at 25°C		355
Free fatty acid (%)		0.68
Ash (%)		1.12
Stability		0.K
Corrosion		0.K

* For both condensations, time was 6 hr, temperature was 80-130°C, and 5% of $AlCl_3$ was used

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Table XXIV(B)36
COMPOSITION AND PROPERTIES
(MAGNETO GREASE)

Properties of Materials		Naphthalene and benzene condensation
Conditions of Synthesis*	Materials $AlCl_3$ (%) ..... 4 Temp (°C) ..... 80-140 Time (hrs) 6	Cracked distillate of wax from 150°C-230°C ..... 80 Naphthalene ..... 3 Benzene 17
Viscosity in	at 10°C	631
Redwood No. 1 sec.	" 30°C	214
Aniline point	(°C)	69
Pour point	(°C)	-60
Flash point	(°C)	165

Composition of Grease		
Synthetic oil	(%)	80
Sodium soap of castor oil	(%)	20
Note: mixed well at 200°C, and then quickly cool		

Properties of Grease		
Appearance		light brown color smooth texture
Dropping point (°C)		176.5
	at 25°C	260
Worked consistency	" 0°C	207
	" -40°C	168

* For both condensations, time was 6 hr, temperature was 80-140°C and 4% of $AlCl_3$ was used

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Table XXV(B)36
COMPOSITION AND PROPERTIES
(IMPROVED MAGNETO GREASE)

Properties of Materials		Naphthalene and benzene condensation
Conditions of Synthesis*	Materials	Cracked distillate of wax from 150°C-230°C ..... % ..... 80 Naphthalene ..... 3 Benzene 17
Viscosity in	at 10°C	631
Redwood No. 1 sec.	" 30°C	214
Aniline point	(°C)	69
Pour point	(°C)	-60
Flash point	(°C)	165
Composition of Grease		
Synthetic oil	(%)	80
Sodium soap of castor oil	(%)	18.8
Calcium oleate	(%)	1.0
Glycerine	(%)	0.2
Properties of Grease		
Appearance		light brown color and unguent type
Dropping point	(°C)	165
Worked consistency	at 250°C	259.5
	" 0°C	211
	" -40°C	191
Solidifying point	(°C)	-55
Free alkali	(%)	0.226
Ash	(%)	1.2
Stability		0.K
Corrosion		0.K

* For both condensations, time was 6 hr, temperature was 80-140°C and 4% of $AlCl_3$ was used

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Table XXVI(B)36
COMPOSITION AND PROPERTIES
(MIXED BASE MAGNETO GREASE)

Properties of Materials		Naphthalene and benzene condensation
Conditions of Synthesis*	Material	Cracked distillate boiling from 150°C to 230°C of wax ..... 90 Naphthalene ..... 5 Benzene 5
Viscosity in	at 300C	206
Redwood No. 1 sec.	10°C	602.1
Aniline point	(°C)	94
Flash point	(°C)	163
Pour point	(°C)	-58
Composition of Grease		
Synthetic oil	(%)	77
Sodium-stearate	(%)	7.5
Sodium- oleate	(%)	7.5
Calcium-stearate	(%)	4.93
Calcium- oleate	(%)	4.73
Glycerine	(%)	0.89
Properties of Grease		
Appearance		light brown color and smooth texture
Dropping point	(°C)	649
Worked consistency	at 25°C	230
	at 20°C	179
Free fatty acid	(%)	0.35
Ash	(%)	2.0
Stability		O.K.
Corrosion		O.K.

* For both condensations, time was 6 hr, temperature was 80-130°C and 3% of $AlCl_3$ was used

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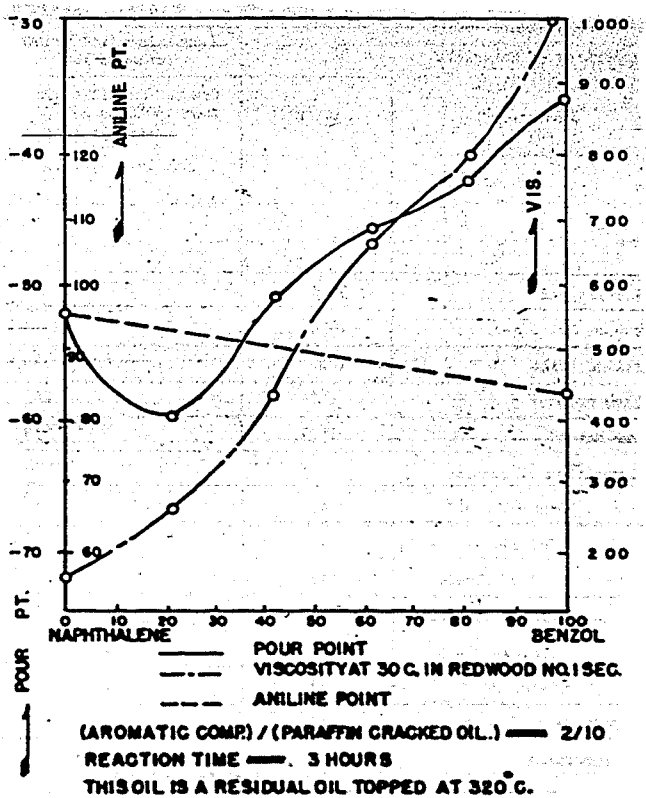

Figure 6(h)36
VISCOSITY POUR POINT AND ANILINE POINT
FOR NAPHTHALENE-BENZENE CONDENSATION OIL