

ENCLOSURE (B)-12

STUDIES ON THE POUR POINT DEPRESSANT
FOR WAX-CONTAINING FUEL OILS

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Research Period: 1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)12

LIST OF TABLES
AND ILLUSTRATIONS

Table	I(B)12	Properties of Sample	Page 106
Table	II(B)12-a	Analysis of Heavy Fuel Oil	Page 107
Table	II(B)12-b	Properties of Aluminium Stearate	Page 107
Table	III(B)12	Effect of Aluminium Stearate on Lowering Pour Point for Heavy Fuel Oil	Page 108
Table	IV(B)12	Determination of the Effect of Mixing Temperature on Pour Point Stability for Fuels Compounded with Aluminium Stearate	Page 108
Table	V(B)12	Tests of Various Aluminium Soaps	Page 109
Figure	1(B)12	Relationship Between Pour Point and Preheating Temperature	Page 110
Figure	2(B)12	Relationship Between Pour Point and Preheating Temperature	Page 111
Figure	3(B)12	Relationship Between Pour Point and Preheating Temperature	Page 112
Figure	4(B)12	Relationship Between Pour Point and Preheating Temperature	Page 113
Figure	5(B)12	Effect of Wax on Pour Point	Page 114
Figure	6(B)12	Effect of Aluminium Stearate on Pour Point	Page 115
Figure	7(B)12	Production of Aluminium Stearate	Page 116

ENCLOSURE (B)12

SUMMARY

From the results of studies on the pour point depressants for the wax-containing fuel oils, it was found that aluminium stearate was most effective. Fuel oils containing 5-10% of wax had a pour point of +15°C. By adding a small quantity of aluminium stearate, such as 0.5 to 1.0%, to this fuel oil, its pour point could be easily depressed below zero degree C.

As the raw material for the manufacture of aluminium stearate, saturated fatty acids whose carbon atom numbers were above eighteen were found to be the best, and it was recognized that the longer the carbon chain, the better result was obtained; however, the effect of aluminium soaps on the pour point of fuel oil depended mainly upon the composition of the fuel oils.

Aluminium stearate was produced on a commercial scale and it was used to some extent by some petroleum companies. It was used (but not produced) by the Navy in the winter of 1944-1945. The cost of aluminium stearate was approximately 1000 yen/ton in 1944.

I. INTRODUCTIONA. History of Project

In April 1943, it was found that a wax-containing fuel oil which was fluid in the tropical zone sometimes suddenly lost its fluidity at lower temperatures during loading in the oil tank.

As Sachanen already has pointed out, the solidification temperature of oils varies with the temperature to which the oils were preheated, and that the higher the preheating temperature, the greater the depression of the solidification point, which, however, rises to its original value in storage. It was necessary, therefore, to find some means of depressing the pour point permanently to 0°C. The following methods were considered:

- (1) Dewaxing
- (2) Cracking of wax-containing fuel oils
- (3) Dilution with low pour point fuel oil
- (4) Addition of pour point depressant

Studies were directed only toward the use of pour point depressants. At first the usual pour point depressants were examined, e.g. "Santo pour", and it was found that they were superior for refined lubricating oils but not effective for heavy fuel oils which contained the asphaltic substance. Considering its colloidal properties, the depression of pour point may be due to the prevention of wax crystal growth and monople soap which was prepared from Kapokseed oil by sulphonation, and, following neutralization, was tested for its effect on the pour point. This soap was fairly effective and hence it was concluded that more metallic soaps, should be investigated. As a result, aluminium stearate was found the best pour point depressant in June, 1943.

B. Key Personnel Working on Project

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ENCLOSURE (B)12

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II. DETAILED DESCRIPTION

A. Variation of pour point of wax-containing fuel oils with their preheating temperature is as follows:

1. A wax-containing fuel oil was diluted with 10 volumes of dichlorethane and filtered at -21°C . Wax and dewaxed oil, thus obtained, were mixed again in various proportions and the pour points were measured. See Figure I(B)12.

As shown in Figure 1(B)12, the pour point of dewaxed oil did not change with the preheating temperature, but wax-containing oil changed abnormally.

2. Normal heptane and sweated wax were mixed in various proportions and the pour points were measured. As shown in Figure 2(B)12, the variation of pour point was not observed.

3. The above mentioned solution of wax and normal heptane was mixed with several amounts of asphalt obtained from Tarakan crude oil by topping to 300°C at 1mm, and the pour points were then measured. As shown in Figure 2(B)12, the abnormality of pour point was observed in curves 2 and 3 of asphalt and wax-containing oil.

4. Sanga Sanga topped heavy oil and Tarakan crude oil were mixed in various proportions, and to these mixtures prepared "Santopour" was added. The results are shown in Figure 4(B)12. Prepared "Santopour" had some effect, but it was far from excellent. One per cent. of monopole soap which was prepared from Kapok seed oil by sulphonation, followed by neutralization, was added to the heavy fuel oil which had -19°C . pour point. The pour point was lowered to -18°C , but on repeating the pour point test it rose to 1°C . From this it seemed that its effect was considerably changed due to change in crystal structure with heating and cooling.

B. Effect of aluminium stearate on pour point of wax-containing fuel oil is as follows:

Tarakan fuel oil which contained no wax had a pour point of 135°C . To this a wax obtained from Sanga Sanga crude oil in South Borneo and melting at 49°C was added in various proportions and their pour points determined.

As shown in Figure 5(B)12, when the content of the 56°C wax was restricted to 7%, and in the case of 49°C wax, to 11%, aluminium stearate was distinctly effective in depressing the pour point of oil. Also, the melting point of the wax had a marked effect on the pour point.

C. Effect of aluminium stearate on the pour point of wax-containing fuel oil which was diluted with lower pour point light oil as follows:

The properties of sample used are shown in Table I(B)12 and Table II(B)12. As shown in Table III(B)12 and in Figure 6(B)12, it was observed that a fuel oil having a pour point below 0°C and not subject to change with preheating was obtainable by blending with 30% of light oil and 0.5% of aluminium stearate. By diluting with the lower pour point light oil, the

ENCLOSURE (B)12

wax content of the fuel oil was reduced to a range where the pour point depressant was very effective.

D. Determination of the necessary temperature to dissolve aluminium stearate completely in fuel oils was arrived at as follows:

0.5 grams of aluminium stearate was dissolved completely, in 30 grams of a light oil at 80°C. This solution was mixed with 70 grams of fuel oil heated at the following mixing temperatures and the pour points after preheating at 40°C. As shown in Table IV(B)12, mixing at 0-60°C, the pour point rose gradually with repeated pour point test, indicating that the mixing temperature should be above 80°C.

E. Preparation of Aluminium Stearate.

Aluminium soaps prepared from hydrogenated palm oil, soy bean oil, sardine oil, and rape oil were tested. The results are shown in Table V(B)12. Of these, aluminium soap of hydrogenated rape oil was the best.

Aluminium stearate was prepared from hydrogenated soy bean oil by the ordinary double decomposition method given in Figure 7(B)12.

III. CONCLUSION

The pour point of wax-containing fuel oil could be depressed to a considerable degree by the limitation of wax content to about 15% and by adding a small amount of aluminium stearate. With this method, the wax-containing fuel became usable in the winter season in Japan, but was utilized only by the oil companies, including Mitsubishi and Showa Petroleum Oil Companies. This method was not used by the Navy.

ENCLOSURE (B)12

Table I(B)12
PROPERTIES OF SAMPLE

Properties	Heavy fuel oil	Light oil
Specific gravity (d ₄ ²⁵)	0.8854	0.8364
Flashing point (°C)	78	41
Pour point (°C)	21	-14
Conradson carbon (%)	2.4	0.03
Viscosity at 30°C (R-1)	69.2	30.5
Water content (%)	1.1	0
Distillation test		
I.B.P. (°C)	95	110
5 (Vol %)	166	180
10	217	
20	238	199
30	250	210
40	269	220
50	283	228
60	318	232
70	332	241
80	349	253
90	323	263

ENCLOSURE (B)12

Table II(B)12-a
ANALYSIS OF HEAVY FUEL OIL

No	Fraction(°C)	Yield(weight %)	Pour Point(°C)
1	95-292	55	-10
2	292-297/4mm	37.2	
	oil part	8.4	+17
	wax part	28.8	+40
3	297/4mm -	6.3	+115
4	loss	1.3	

Table II(B)12-b
PROPERTIES OF ALUMINIUM STEARATE

Free fatty acid (%)	43.8
Combined fatty acid (%)	50.0
Ash (%)	9.9
Free H ₂ SO ₄	0.5
Water content	13
Na ₂ SO ₄	4.6
Pure Aluminium stearate (%)	51.6
Iron stearate	2.2
Weight of 100 (gm)	0.25

ENCLOSURE (B)12

Table III(B)12
EFFECT OF ALUMINIUM STEARATE ON LOWERING POUR POINT FOR HEAVY FUEL OIL

Proportion of Mixing (wt %)			Pour Point (°C) at each preliminary temp.		
Heavy Fuel Oil	Light Oil	Aluminium Stearate	30°C	40°C	50°C
100	0	0	18	21	18
80	20	0	12	16	13
80	20	0.5	-5	15	1
70	30	0	-11	14	11
70	30	0.5	-17	-5	-14
60	40	0	10	12	4
60	40	0.5	-21	-18	-25
50	50	0	10	0	0
50	50	0.5	-31	-30	-32
0	100	0	-14	-14	-14

Table IV(B)12
DETERMINATION OF THE EFFECT OF MIXING TEMPERATURE ON POUR POINT STABILITY FOR FUELS COMPOUNDED WITH ALUMINIUM STEARATE

Mixing temp. (°C)*		Test Number					
		1	2	3	4	5	6
Pour Point (°C)	20	-11	-13	-11	-8	-7	-5
	40	-14	-14	-13	-9	-6	-8
	60	-18	-17	-17	-15	-14	-10
	80	-23	-23	-24	-23	-23	-23
Without Aluminium Stearate		*15	—	—	—	—	—
Time elapsed (Day)		0	0	0	3	4	4

*Preliminary temperature in each test was 40 °C.

ENCLOSURE (B)12

Table V(B)12
TESTS OF VARIOUS ALUMINIUM SOAPS

1	Properties of Fatty Acid			Aluminium Soaps		Pour Point (°C)				
	Fatty Acid	Iodine Value	Melting Point (°C)	Water Content (%)	Quantity Used (%)	Preheating at Next Temperature (°C)				
						20°C	30°C	40°C	50°C	
2	Hydrogenated				0	+7	+16	+17	+15	
3				0.8	1.0	-15	-22	-20	-23	
4				10.1	1.1	-16	-21	-21	-21	
5	soy			22.7	1.3	-18	-21	-20	-22	
6				37.3	1.6	-17	-19	-17	-19	
7	bean	14.4	62	1.5	0.5		-7	-13	-15	
8				6.0	63.8	0.04	0.5	-6	-6	-16
9	oil	6.0	63.8	0.04	0.2		+17	+18	+15	
10				14.3	51.3	0.04	0.5	-19	-14	-18
11				5.7	53.4	0.77	0.5	-15	-13	-16
12	Hydrogenated sardine oil	5.7	53.4	0.77	0.2		-3	+17	-4	
13				18.9	59.1	0.31	0.5	-15	-16	-18
14	Hydrogenated rapeseed oil	18.9	59.1	0.31	0.2		-12	-1	-13	
15				3.2	58.0	3.8	0.5	11	-5	-5

ENCLOSURE (B)12

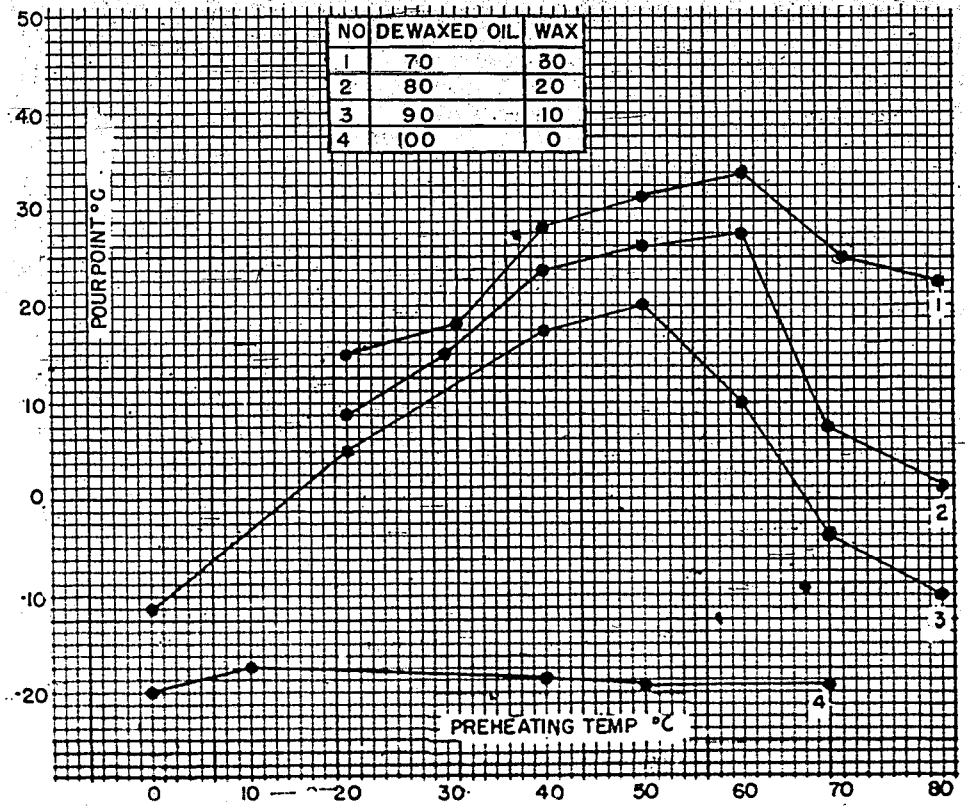


Figure 1 (B)12
RELATIONSHIP BETWEEN POUR POINT
AND PREHEATING TEMPERATURE

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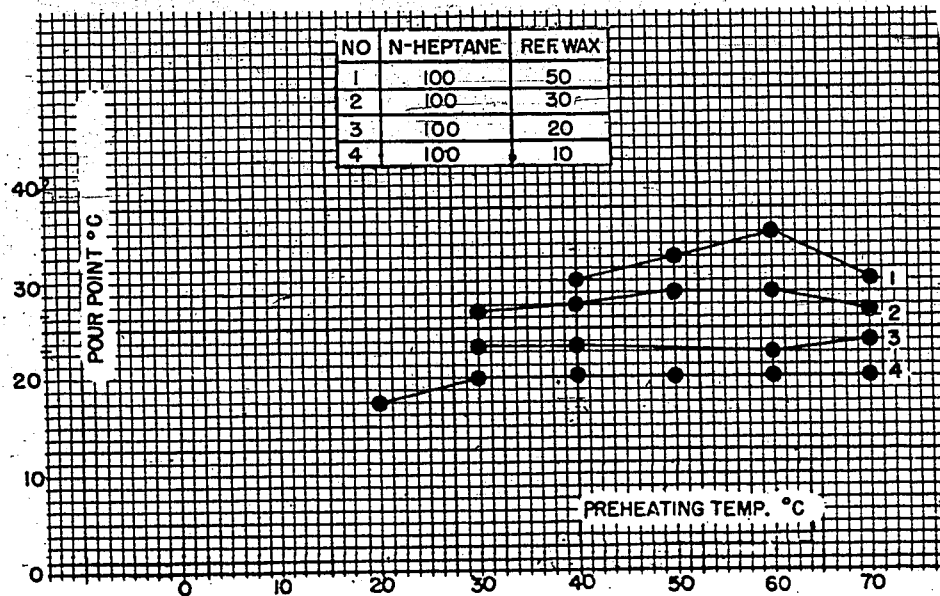


Figure 2 (B)12
-RELATIONSHIP BETWEEN POUR POINT
AND PREHEATING TEMPERATURE

ENCLOSURE (B) 12

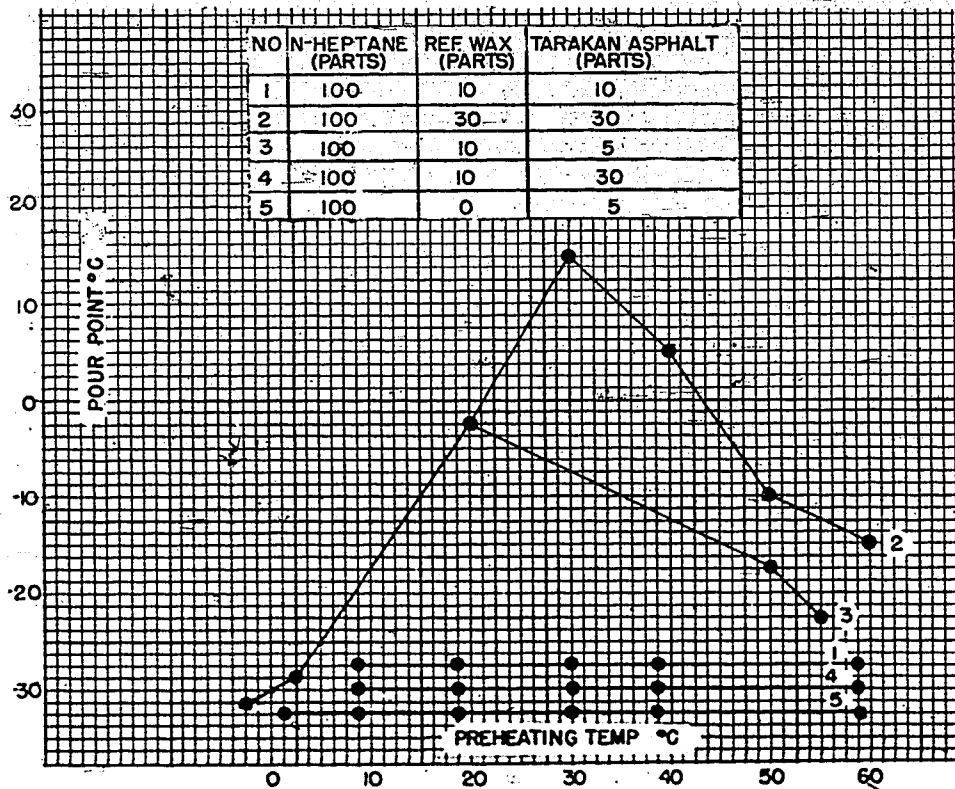


Figure 3 (B) 12
RELATIONSHIP BETWEEN POUR POINT
AND PREHEATING TEMPERATURE

ENCLOSURE (B)12

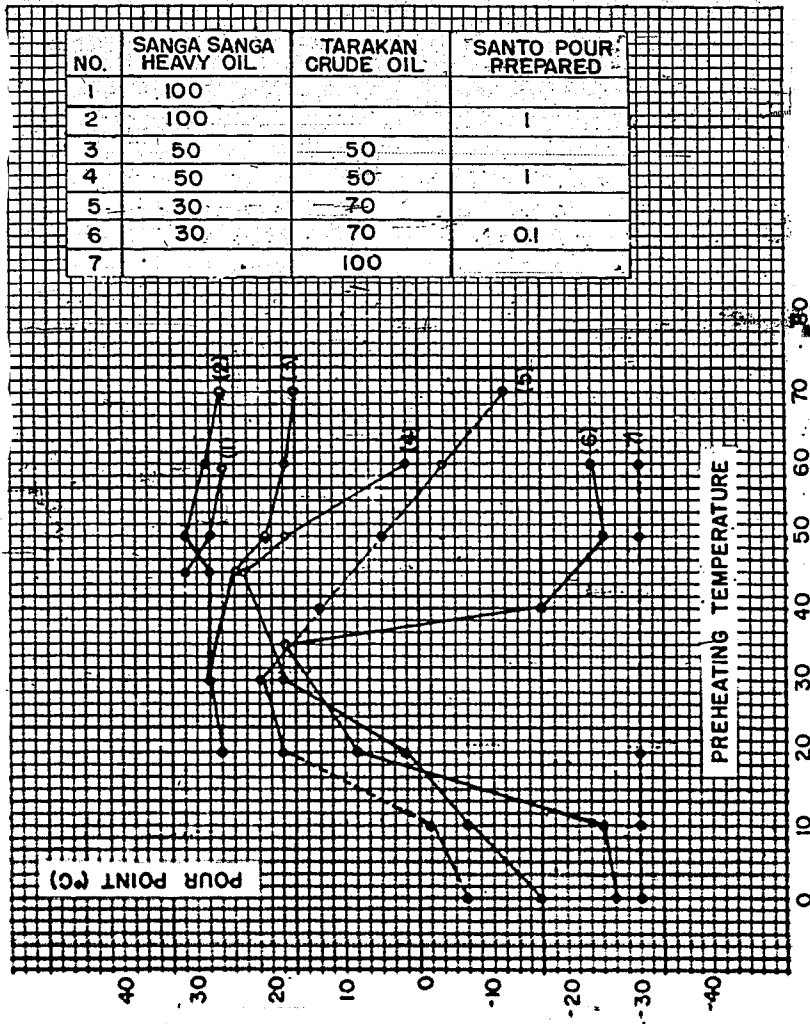


Figure 4 (R)12
RELATIONSHIP BETWEEN POUR POINT
AND PREHEATING TEMPERATURE

ENCLOSURE (B)12

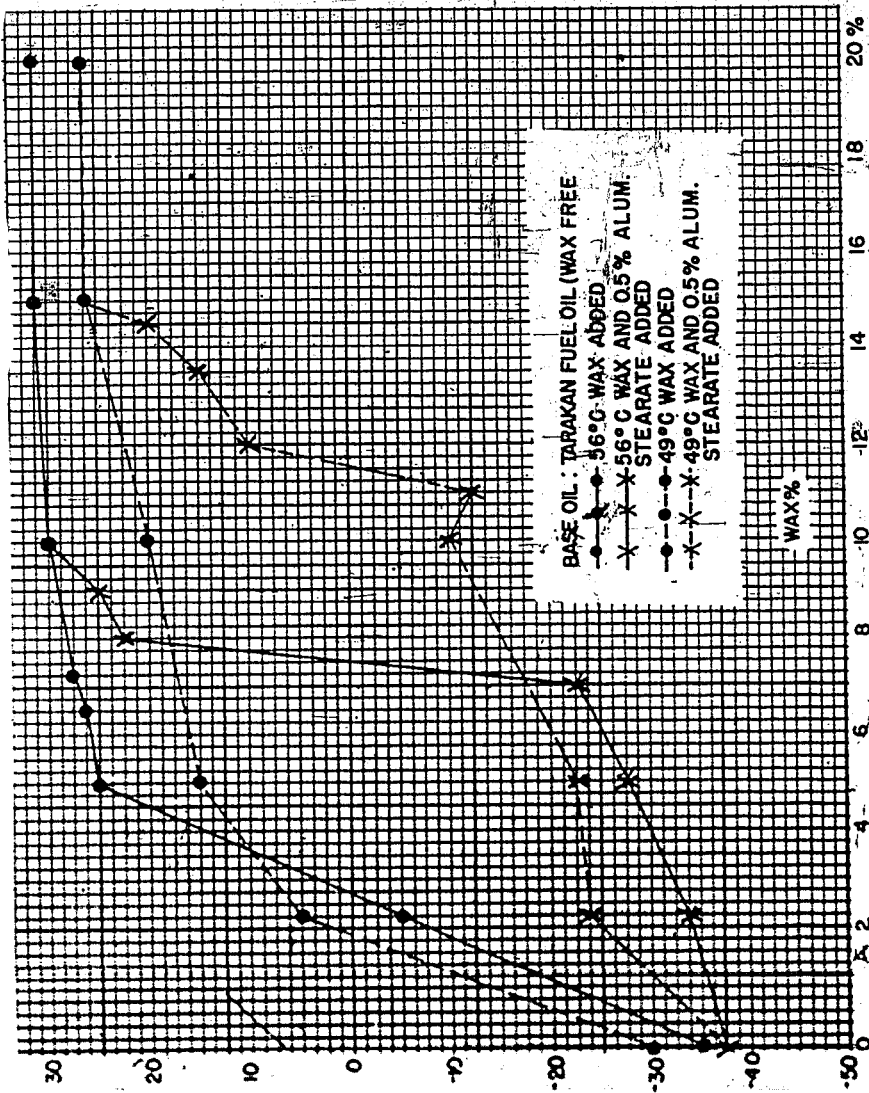


Figure 5 (B)12
EFFECT OF WAX ON POUR POINT

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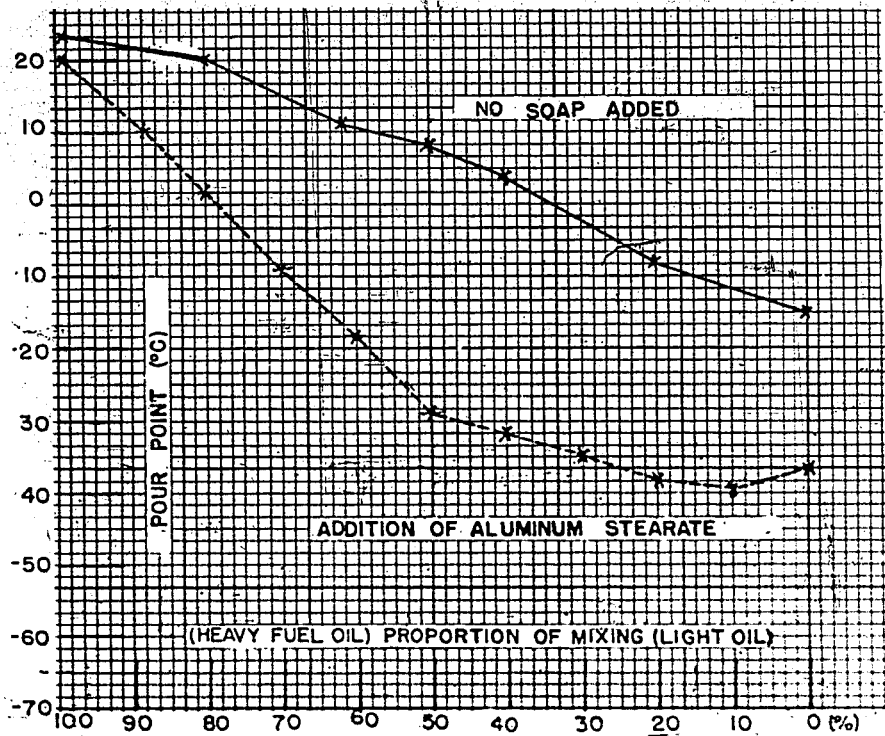


Figure 6 (b) 12
EFFECT OF ALUMINUM STEARATE
ON POUR POINT

ENCLOSURE (B)12

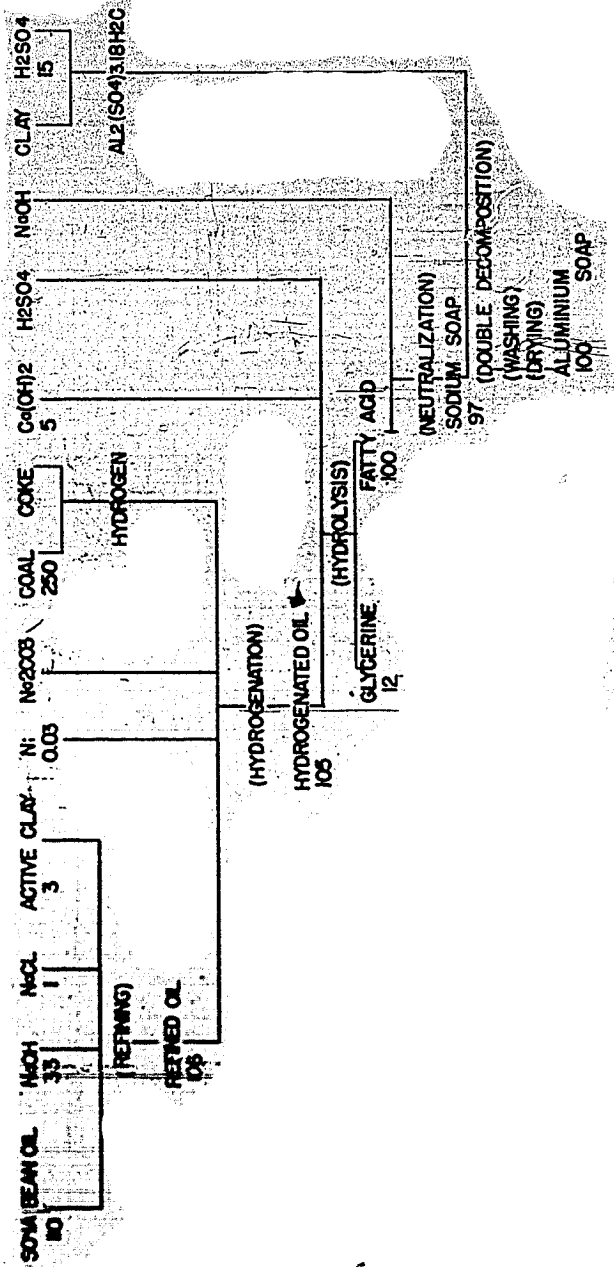


Figure 7 (B)12
PRODUCTION OF ALUMINIUM STEARATE