VARIABLES AFFECTING THE POUR-POINT DEPRESSING PROPERTY OF THE ALKYLATED PRODUCT OF INDIGENOUS MICROCRYSTALLINE WAX AND NAPHTHALENE

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(Received June 9, 1971)

Abstract. Mineral oils such as furnace, lubricating and jute-batching oils, tend to freeze in winter season which makes their pumping difficult. In order to facilitate pumping, their pour-point is lowered by adding a pour-point depressant in small amounts.

A number of pour-point depressants partly based on indigenous raw materials such as paraffin-waxes, chlorine and certain aromatic compounds have been prepared in these laboratories. One of the condensation products obtained from microcrystalline-wax (molecular formula $C_{40}H_{82}$) and naphthalene, is capable of depressing the pour-point of the jute-batching oil (JBO) from 65°F to less than 20°F.

The variables which effect the degree of condensation and make the end product useful as pour-point depressant are temperature, time of reaction, amount of chlorine in the chlorinated-wax and the proportion of reactants and catalyst. The study of these variables forms the basis of the present investigation.

Heavy mineral oils have a tendency to freeze in winter season which makes their pumping difficult. In order to overcome this difficulty, these oils are mixed with additives known as pour-point depressants (PPD) in small proportions which depresses their pour-point without changing the physical properties of the oils. The two pour-point depressants namely the Paraflow and Amoco, currently in use with the local refineries are being imported. Paraflow[1,2] is a condensation product of a chlorinated-wax and naphthalene, while Amoco is a higher polymeric type compound, both of unknown composition.

In an attempt to prepare Paraflow type of compounds, a series of experiments were carried out on indigenous microcrystalline-wax which was first chlorinated and then condensed with a number of cyclic compounds namely benzene, xylenes, naphthalene and phenol etc. in the presence of a catalytic agent, $AlCl_3$. Of all the condensed products, the one obtained from naphthalene showed satisfactory results (Table 1).

Though a considerable amount of work on alkylation condensation between the chlorinated-wax and naphthalene has been done, only a limited number of workers have reported the details of the effect of the variables involved in the process namely temperature, duration of reaction, percentage of chlorine in the chlorinated-wax and finally the proportion of the reactants. MacLaren[3] carried out the alkylation at a temperature of 55°C or higher without giving any reason thereto. Farbenind,[4] Ivanova[5] Reiff and Badertscher,[6] and Lieber and Dean[7] have stated that the products could be prepared at different temperatures varying between 5–175°C but they too did not indicate the significance of using such a wide range of temperature and its specific effect on the product.

Again relatively less attention appears to have been paid to the study of the effect of time on the condensation reaction. When the evolution of HCl ceases, it is generally assumed that the reaction is complete, but distinctly better results (as pour-point depressant) have been obtained when the product is kept at an elevated temperature (rather range of temperature) for a definite period of time. In this context different workers have used different periods to complete the reaction. Farebenind[4] for example completed the reaction in 5 hr while Ivanova[5] obtained a condensation product in 2 hr at 5°C. Likhushin and Geiman[8] have also indicated the completion of reaction in 2 hr but at 65°C, whereas Lieber and Cashman[9] obtained the final product by refluxing the reactants for 2–12 hr. These varying conditions may be attributed either to the type of the wax or its degree of chlorination.

The amount of chlorine in the chlorinated-wax has a decisive influence on the effectiveness of the product as a pour-point depressant. This point has also been emphasised by other workers, Frolich,[10] Lieber and Dean,[7] for example, reported to have obtained good results by using chlorinated-waxes with chlorine ranging from 10 to 20%. Ramayya and Khaiman,[11] and also Reiff and Badertscher,[6] Ivanova,[5] and Christ-

TABLE 1. EFFECT OF DIFFERENT ALKYLATED PRODUCTS ON THE POUR–POINT OF JUTE-BATCHING OIL (JBO). (POUR-POINT OF JBO=65°F).

Alkylated product (A)	Percentage of (A) in (JBO) (w/v)	Pour-point of JBO (°F)
Benzene	5% and less	55
Mixed xylenes	,, ,, ,,	55
m-Xylene	,, ,, ,,	60
o-Xylene	,, ,, ,,	55
p-Xylene	,, ,, ,,	55
Phenol	,, ,, ,,	55
Naphthalene	5%	Less than 20
Petkolin	,,	45
Toluene	Product not soluble	
Anthracene	4%	40

man and Geig[13] particularly stressed that the amount of chlorine in the chlorinated-wax should remain between 13–15%. Lieber[12] prepared a product with 11% chlorine in long chain aliphatic compounds having at least 10 carbon atoms. Simply stating the percentage of chlorine without giving the molecular weight of the wax will limit the usefulness of the results. It, therefore, seems imperative to know the percentage of chlorine in relation to the molecular weight of the wax used in the synthesis of the pour-point depressant. In order to make the process more economical, without the wastage of the reactants, it is desirable that the ratio between the reactants be determined experimentally. Farbenind,[4] for example, used naphthalene and chlorinated-wax in a mol ratio of 1:1 whereas Christman and Geig,[13] and Michel and coworkers[14] kept it at 1:6. Molar proportions of 1:2–6 has been used by Reiff and Badertscher,[6] and Lieber and Dean.[7] Thus it will be seen that the molar ratio given by the different workers changes from 1:1 to 1:6 without mentioning the type of the wax used and as such they are not useful for predicting a suitable molar ratio for a given wax..

Farbenind[4] used 25% $AlCl_3$ for the reaction. Later workers like Reiff and Badertscher,[6] and Christman and Geig[13] used 3–10% of $AlCl_3$ based on the amount of the chlorinated-wax. A relationship between the reactants and catalyst was worked out at Standard Oil Develop. Co.[15] which states that the catalyst should be between 0.5–5.0% by weight of the halogenated material and the arithematic product of the percentage of the catalyst (based on the weight of the chlorinated-wax) times the square of the percentage by weight of halogen in chlorinated material, should be *at least 400*. Accordingly, the figure, worked out by the present workers, comes to about 1500. The amount of the catalyst used in the present case was 15% of the weight of chlorinated-wax used.

Apparatus and Procedure

Microcrystalline-wax $C_{40}H_{82}$,[16] melting point range 52–54.5°C was chlorinated in a vertical-coil condenser at a temperature range of 60–80°C to a density of 0.9–0.905 g/ml.

The conventional alkylation apparatus as shown in the Fig. 1, consists of a 1 lit. 3-necked round bottom flask(F), a coiled condenser (C) fitted with moisture-trap was mounted on one of its necks and a thermometer(T) is fitted onto the second neck, while a glass-stirrer with mercury-seal (MS) is mounted on the third neck. The thermometer pocket was also used as an inlet for $AlCl_3$. About 50 g of naphthalene and 100 g of chlorinated-wax, dissolved in 150 ml CCl_4, are introduced in the flask. The apparatus was quickly assembled and the flask lowered in an ice-bath. $AlCl_3$ (15 g) is then gradually added at a rate of 1–2 g/min. When the addition of $AlCl_3$ is complete, and the violence of the reaction subsided, the ice-bath is replaced by a heating mantle and the temperature is gradually raised. Heating is continued till the final temperature of 80°C is reached, at which the contents are kept for the rest of the period of reaction.
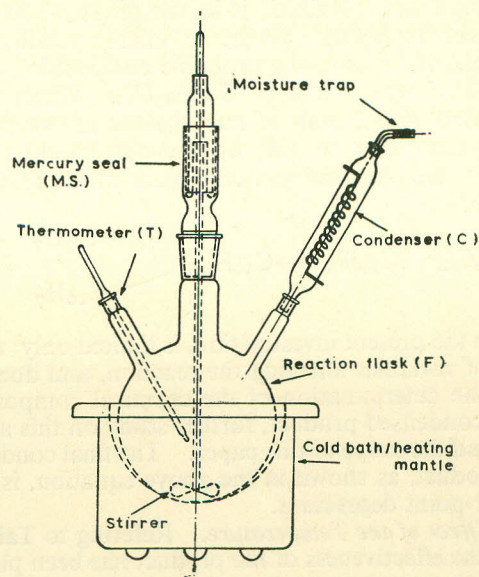

Fig. 1. Alkylation apparatus.

Using the above procedure, the method of study of the variables is as described below:

(1) *Temperature of the Reaction.* The effect of temperature was studied over a temperature range of 30–80°C, with a temperature interval of 15°C.

(2) *Time of Reaction.* Reaction time over a period of 8–24 hr with time interval of 8 hr, was studied.

(3) *Amount of Chlorine in the Chlorinated-wax.* The wax was chlorinated to a density range of 0.875–1.125 and samples of density 0.875, 0.900, 0.925, 0.950, 0.975 and 1.125 corresponding to 7.40, 10.7, 12.28, 16.6, 23.0 and 30.0% of chlorine, were collected for condensation with naphthalene. The temperature and time of reaction were kept at 80°C and 16 hr respectively.

(4) *Amount of the Reactants.* In order to fix the ratio between naphthalene and the chlorinated-wax, the amount of chlorinated-wax was varied from 0.5 to 4 times the weight of naphthalene, the other conditions remaining constant.

The amount of catalyst used, determined on the basis of the amount of the chlorinated-wax, was varied between 5–30% of the amount of chlorinated-wax and its effect studied on the final product.

(5) *Procedure for Purification.* After the completion of the reaction, the products were cooled and then dissolved in CCl_4 or petroleum-cut (b.p. 80–150°C). In order to break the aluminium chloride-wax complex, the product was either agitated with cold concentrated hydrochloric acid or 1–2% solution of sodium hydroxide or sodium sulphate for 1 hr and then allowed to settle in a separating funnel. The product was then washed with distilled water to remove $AlCl_3$ and dried over water-bath and finally in an air-oven at 110°C.

Results and Discussion

The optimum amount of chlorine in the chlorinated-wax, where best results in terms of pour-point

depression are obtained, is in the range of 10–11%. Since the molecular weight of microcrystalline-wax is $C_{40}H_{82}$, therefore, the probable composition of the chlorinated wax would be $C_{40}H_{80}Cl_2$. When this is condensed with 2 mols of naphthalene in presence of $AlCl_3$, according to the worked-out conditions of reaction, the reaction may take place in the following manner:

$$C_{40}H_{80}Cl_2 + 2C_{10}H_8 \longrightarrow C_{40}H_{80} \Big\langle \begin{array}{c} C_{10}H_7 \\ C_{10}H_7 \end{array} + 2HCl$$
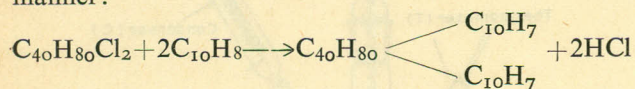
Since the present investigation, is limited only to the study of variables affecting the reaction, and does not cover the determination of the chemical composition of the condensed product, further study on this aspect is beyond the scope of this paper. The final condensation product, as shown in the above equation, is used as pour-point depressant.

(1) *Effect of the Temperature.* Refering to Table 2, where the effectiveness of the product has been plotted against the temperature, it can be seen that the reaction carried out at lower temperatures, that is less than 30°C, does not yield a product of the desired effectiveness, most probably due to incomplete degree of condensation. As the reaction temperature rises, the effectiveness of the product also rises and is reported to be maximum at 80°C where the final product, if added in 5% or less concentrations, depresses the pour-point of JBO from 65 to less than 20°F. Higher refluxing temperatures, namely 110°C and above, do not improve the product because almost the same results have been obtained as in the case of 80°C. Though the precise effect of temperature may not be known but one effect is markedly apparent that it definitely helps in bringing about a complete condensation between the chlorinated-wax and naphthalene, i.e. a complete substitution of the Cl atoms present in the chlorinated-wax by the naphthalene ring.

(2) *Effect of the Duration of Reaction.* The duration of the reaction which would give a satisfactory end-product, was studied by keeping the other variable constants namely temperature, amount of catalyst and the ratio of reactants. The results indicate that the end-product obtained particularly at 16 hr gives the best results, i.e. with 5% concentration the pour-point of the JBO is depressed from 65 to <20°F (Table 3). Further, increase in the time of reaction, i.e. up to 24 hr does not improve upon the pour-point depressing properties of the end-product. Thus it would be seen that 16 hr is the optimum duration of reaction for obtaining a satisfactory product.

(3) *Pour-Point Depressing Property as Function of the Percentage of Chlorine in the Chlorinated-wax.* Of all the variables studied, the percentage of the chlorine in the chlorinated-wax is perhaps the most important. The chlorinated-wax with Cl_2 percentage varying from 7.4 to 30 was condensed with naphthalene and tested for the pour-point depressing property. The results thus obtained are presented in Fig. 2, where the pour-point of JBO has been shown as a function of the percentage of chlorine present in the

TABLE 2. EFFECT OF THE TEMPERATURE OF REACTION.

(Duration of reaction, 16 hr; ratio of the reactants (naphthalene : Cl-wax : $AlCl_3$), 1:2 (:2 : 0.3); original pour-point of JBO, 65°F; solvent CCl_4)

Temperature of reaction (0°C)	Active component (%)	Pour-point of JBO (°F)
30	5%	45
45	”	40
60	”	25
80	”	<20
110	”	<20

TABLE 3. EFFECT OF THE TIME OF REACTION.

(Ratio of reactant; 1:2 (:0.3); temperature of reaction, 80°C; original pour-point of JBO 65°F; solvent used CCl_4)

Time of reaction (hr)	Percentage of the PPD	Pour-point of JBO (°F).
8	(i) 5	65
16	(i) 5	<20
	(ii) 4	<20
	(iii) 3	20
	(iv) 2	25
	(v) 1	45
24	(i) 5	<20
	(ii) 4	<20
	(iii) 3	20
	(iv) 2	25
	(v) 1	45

chlorinated-wax. The curve which resembles an inverted parabola, shows a maximum depression in pour-point at the 'hump' and thereafter it falls off rapidly. The 'hump', i.e. the maxima corresponds to a chlorine contents of about 10.7% which apparently compares well with the findings of some of the workers as discussed earlier, but since the molecular weights of the waxes used by most of the workers is not known, this comparison simply becomes meaning less.

(4) *Pour-Point Depressant as Function of the Proportion of the Reactants and the Catalyst.* In order to make the process economical especially when the exact molecular weight of the chlorinated-wax is doubtful, it is imperative that their individual amount be determined experimentally. Consequently the effect of the amount of the chlorinated-wax, and the catalyst have been studied on the effectiveness of the final product, for a given amount of naphthalene.

(4a) *The Effect of the Ratio of Naphthalene and the Chlorinated-wax in the Reaction Mixture.* Referring to Table 4, it will be seen that by varying the ratio of naphthalene to chlorinated-wax from 1:0.5 to 4.0 for a given amount of $AlCl_3(7.5 g)$ the best products from the point of pour-point depressing property, are those which are obtained when the ratio
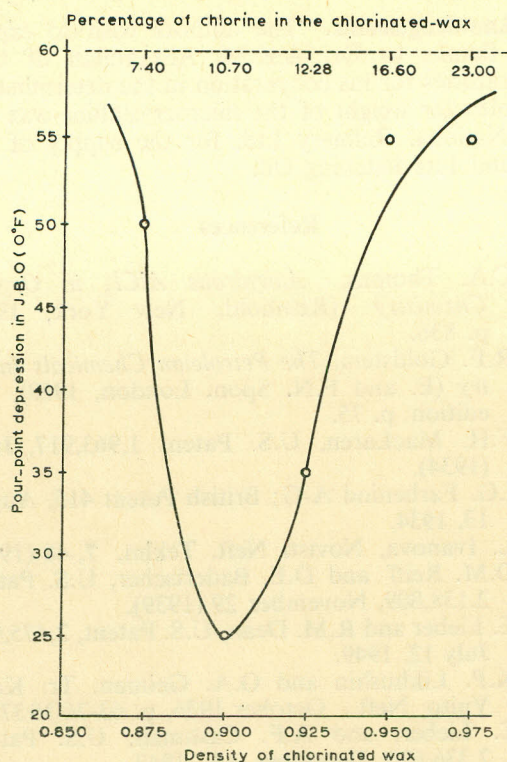
Percentage of chlorine in the chlorinated-wax

Fig. 2. Pour-point depression in jute batching oil (JBO) vs. density of chlorinated-wax (or chlorine percentage in chlorinated-wax)

(by weight) of naphthalene to the chlorinated-wax and Al Cl$_3$ is 1:2:0.3. The effect of this ratio is also shown in Fig. 3. In this figure, the minima occurs at a point where the naphthalene and the chlorinated-wax used is in the ratio of 1:2, the corresponding depression in the pour-point of the JBO being 25°F.

(4b) *Pour-Point Depression as Function of the Amount of the Catalyst.* For given conditions of experiment the amount of the catalyst used has been varied between 2.5 and 15 g which shows that the best results are obtained when 7.5 g i.e. 15% catalyst, has been used (Table 5). Further the end products as recommended by different authors, have been treated with HCl, NaOH and Na$_2$SO$_4$ but no marked effect of this treatment has been noticed on the end-product which may also be seen in Tables 4 and 5.

Conclusion

Microcrystalline-wax of the composition shown in the present investigation when con densed with naphthalene according to the worked-out conditions, shows promising results as a pour-point depressant, while the condensed products with other aromatics (Table 1) do not give satisfactory results.

Further work on evolving economic process of manufacture and an increase in the effectiveness of the depressant is in progress.
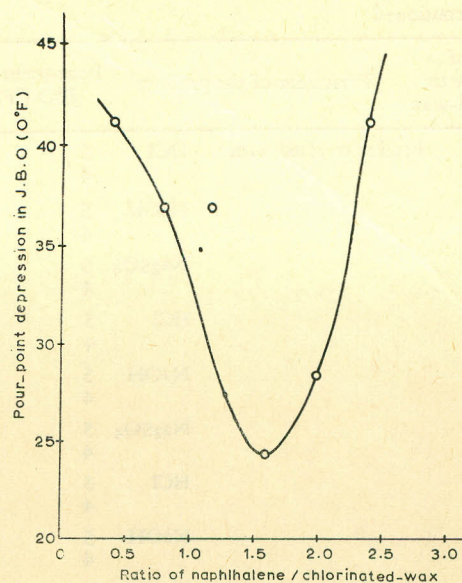

Fig. 3. Pour-point depression in jute batching oil (JBO) vs. ratio of naphthalene/chlorinated-wax in the reaction mixture.

TABLE 4. PROPORTION OF CHLORINATED-WAX IN THE REACTANTS.

Reaction time, 16 hr; reaction temperature, 80°C; amount of naphthalene, 25.0 g; amount of AlCl$_3$, 7.5 g; original pour-point of JBO 65°F.

Ratio of Naphthalene to chlorinated-wax	Treatment of the product		Pour-point of JBO (°F)
1:0.5	Product treated with	HCl	5% sol 55
			4 60
		NaOH	5 45
			4 45
		Na$_2$SO$_4$	5 40
			4 45
1:1.0	Product treated with	HCl	5% sol 55
			4 55
		NaOH	5 40
			4 45
		Na$_2$SO$_4$	5 40
			4 45
1:1.5		HCl	5 40
			4 40
		NaOH	5 35
			4 35
		Na$_2$SO$_4$	5 40
			4 40
1:2.0		HCl	5 30
			4 35
		NaOH	5 25
			4 30
		Na$_2$SO$_4$	5 25
			4 30

Table 4. continued

Ratio of naphthalene to chlorinated-wax	Treatment of the product		Pour-point of JBO (°F)	
1:2.5	Produc treacted with	HCl	5	30
			4	35
		NaOH	5	30
			4	35
		Na$_2$SO$_4$	5	35
			4	40
1:3.0		HCl	5	55
			4	55
		NaOH	5	45
			4	50
		Na$_2$SO$_4$	5	45
			4	50
1:4.0		HCl	5	40
			4	45
		NaOH	5	30
			4	35
		Na$_2$SO$_4$	5	45
			4	45

TABLE 5.   AMOUNT OF CATALYST IN THE REACTANTS.

Amount of catalyst	Final treatment of the product		Pour-point of JBO (°F)	
2.5 g (5.0%)	Product treated with	HCl	5% sol	65
		NaOH		65
		Na$_2$O$_4$S		65
5.0 g (10.0%)		HCl		65
		NaOH		55
		Na$_2$SO$_4$		55
7.5 g (15.0%)		HCl		25
		NaOH		30
		Na$_2$SO$_4$		20
10.0 g (20.0%)		HCl		30
		NaOH		40
		Na$_2$SO$_4$		30–35
15.0 g (30.0%)		HCl		65
		NaOH		65
		Na$_2$SO$_4$		65

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