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METHOD FOR PRODUCING WAX MODIFYING AGENTS

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The present invention relates to an improved method for producing wax modifying agents for use in waxy lubricating oils as pour depressants and as crystallization inhibitors to be employed in the process of separating wax from mineral oils. The invention will be understood from the following description:

Wax modifying agents are now produced by condensation of paraffinic compounds having long hydrocarbon chains such as paraffin wax on aromatic hydrocarbons or other cyclic compounds. The reaction is ordinarily conducted by means of Friedel-Craft type catalysts such as aluminum chloride and it is customary to use a diluent during the condensation step. In most cases, petroleum, naphthas, kerosenes and the like have been employed as diluents, but ethylene dichloride and propylene dichloride have also been suggested.

It has been found that the type of solvent employed has a marked effect on the yield and the potency of the wax modifying agent. It has been found to be desirable to employ solvents which are substantially non-reactive with the reactants employed under the conditions prevailing and for this reason saturated aliphatic hydrocarbons were at first preferred since they are the least expensive and are relatively unreactive. On the other hand it was found that when these materials were used as the solvent medium the condensation is accompanied by the simultaneous formation of oil insoluble products. The mechanism of their formation is, as yet, obscure but such oil insoluble materials are of no value as wax modifying agents but on the contrary are undesirable and it is obviously desirable to conduct the condensation in such a way as to avoid such formation. Various expedients have been adopted from time to time to eliminate the formation of oil insoluble materials, for example, the use of increased quantities of the catalyst in operation at more elevated temperatures have been found to decrease the formation of insoluble products but unfortunately these methods are accompanied by a decrease in the potency of the oil soluble fractions as modifying agents. One method of prominence consisted in the use of chlorinated wax of lower chlorine content, for example, below about 11%. Using a wax of this chlorine content and careful adjustment of the amount of catalyst and reaction temperature it is possible to largely eliminate the oil insoluble material but such procedure is accompanied by a decrease in potency, due to the smaller chlorine content of the wax.

The present inventors have found that certain halogenated hydrocarbon solvents during the condensation leads to greatly improved results. On the one hand, these solvents give the least amount of oil insoluble waste materials and, on the other hand, if proper solvents and conditions are employed, products of a high degree of potency can be obtained, even with waxes of high halogen content, and without the production of oil insoluble products. It will be understood that the particular solvent media do not have to be those which are completely incapable of reacting but are such that do not react readily under the conditions prevailing so that they are in effect substantially inert to the reactants. The particular solvent media which are found to best fulfill the requirements belong to two groups; first, aliphatic hydrocarbon derivatives of two or more carbon atoms in which three or more halogen atoms are attached to the same or to adjacent carbon atoms of the molecule. Among such solvents may be specifically mentioned trichlorethane, tetrachlorethane, trichlorethylene, tetrachlorethylene, penta and hexachlorethanes. Similar derivatives of propane, propylene and the butanes and butylenes may also be used, as well as the higher boiling halogenated hydrocarbons, but it is preferable to use the lower boiling derivatives of 2 to 4 carbon atoms since these may be more conveniently separated from the wax modifier and recovered. The chlorinated derivatives of these hydrocarbons are more satisfactory than the derivatives of methane because the latter are more reactive to the reactants under the conditions employed. Saturated solvents such as tetrachlorethane are preferable to tetrachlorethylene, because under the same conditions the former produce products of greater potency. It will be understood that the chlorides are the most desirable because of their cheapness and their stability, but fluorides, bromides and iodides may, of course, be used.

The other group of solvents consist of the halogenated aromatic hydrocarbons. These compounds should contain at least two halogen atoms on the same ring but it is not of great importance whether these halogen atoms are attached to adjacent carbon atoms of the ring. It is preferred to use monocyclic aromatic hydrocarbons, that is to say derivatives of benzol, but the substituted derivatives of naphthalene can also be used. Specific examples of the most desirable compounds are dichlorbenzol, trichlorbenzol, penta or hexa chlorbenzol, di and trichlornaphthalenes.

It will be understood that other halogen atoms may be substituted for the chlorine atoms.

The wax modifying agents are prepared by reaction of at least two types of ingredients. One of these is termed a paraffinic material and among the various paraffinic materials chlorinated paraffin wax, usually containing from 10 to 15% or 20% of chlorine, is preferred. Dechlorinated wax, that is to say the olefins obtained from chlorinated wax, can also be used, but they are less reactive than the chlorine containing compound and for that reason are not so useful. Acid chlorides may also be used where there is a long hydrocarbon chain, for example, having at least 10 or 12 carbon atoms, such as stearyl or oleyl chloride. Chlorinated alcohols, ethers or esters may also be employed in the same way so long as they have relatively long hydrocarbon chains and contain an amount of chlorine comparable to the 10 to 20% of the chlorinated paraffin wax.

The second reactant is a cyclic compound which may be a hydrocarbon such as benzol, naphthalene or anthracene, or a hydroxy aromatic such as a phenol or a naphthol, or an amine such as aniline or naphthylamine may be used. The paraffinic material is used in excess of the aromatic, ordinarily to 100 parts of the chlorinated paraffinic material from 10 to 20 parts of the aromatic are used although there may be considerable variation.

The catalytic agents employed in the condensation are in general the Friedel-Craft catalysts as mentioned above. Aluminum chloride is perhaps the best and the most generally available, but others of the same type can be used such as zinc chloride, iron chloride, aluminum bromide, boron fluoride or titanium fluoride. Ordinarily the catalyst is used in proportion of 1 to 5%, or more, based on the chlorinated paraffinic material.

The reactants may be admixed in any order; for example, the chlorinated or otherwise halogenated wax and the aromatic, say naphthalene, may be mixed with the solvent and the catalyst may then be slowly added as the reaction progresses or, on the other hand, naphthalene and catalyst may be mixed with the solvent and the chlor wax added thereto slowly and the mixture kept in thorough agitation during the reaction. This latter method has marked advantages because it even permits the use of more highly chlorinated waxes, for example waxes containing 15 or even 20% of chlorine or more, and the products produced by such reactions are substantially free from oil insoluble products or, at least, the amount of insoluble product is very greatly reduced over the amount produced by mixing the reactants in any other way. It will be understood that the use of the chlorinated solvents disclosed herein is beneficial for the reaction whatever the particular method or order of adding the reagents, but is particularly beneficial when high chlorine content waxes are used and when the chlorinated wax is added to the mixture of aromatic and catalyst in the manner disclosed above.

The temperature of condensation may vary considerably, preferably from room temperature to about 200° F., the optimum temperatures depending on the particular reactants and to a lesser extent on the particular solvent medium which are used, but in general the optimum is in the range specified and well below the temperature at which the potency of the oil soluble product is found to decrease. Temperature likewise depends to some extent on the amount of catalyst used and on the time of reaction. Ordinarily in the preferred temperature range, the time of reaction to give the most potent product should be less than about six hours, although good pour inhibitors may be obtained at longer times especially where less catalyst is used and where other factors are modified.

The reaction product is preferably finished by hydrolyzing either with acid or alkali in water or alcohol and is washed free of the catalyst sludge.

To illustrate the present invention and to set forth its advantages, the following examples are presented:

Example I

Two condensations were carried out under conditions as closely identical as possible except that in one case no solvent whatever was used and in the other 50 parts by volume of tetrachlorethane was used for 100 parts of chlorinated wax. The proportions of the reactants are as follows in both cases:

	Parts
Chlorinated wax (11% Cl)	100
Napthalene	13.5
Anhydrous aluminum chloride	1.4

The temperature was maintained at 150° F. for a period of three hours and both products were finished in the same way by hydrolyzing the remaining catalyst and withdrawing the sludge.

It was found that the reaction product produced without the use of a solvent was reduced to a final content of about 2½% of an oil insoluble material, while there was no oil insoluble material whatever found in the reaction product made in presence of the chlorinated solvent medium.

During the course of the reaction, samples were removed from the reactor and examined for oil insoluble material present. The following comparative results were obtained:

Time	Formation of oil insoluble material	
	No solvent	50 parts of tetrachlorethane
	Percent	*Percent*
1 hour	25	0
1.5 hours	25	0
2.0 hours	10	0
2.5 hours	2.5	0
3.0 hours	2.5	0

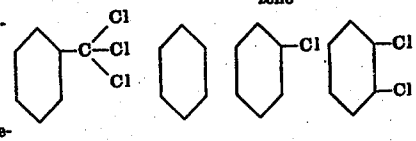
As will be observed, there was no evidence at any time for the presence of oil insoluble material when using tetrachlorethane as solvent.

The oil products produced in each case were very similar but the product made in presence of the solvent was more potent as is shown by the fact that .0375% of the two materials respectively were added to a waxy oil having an original pour point of 30° F., the product made without the solvent depressed the pour point to +15° F., while that made in the presence of the solvent depressed the pour point to 0° F.

Example II

The same experimental procedure was used as in the previous example (No. 1). Here benzotrichloride, benzene, mono-chlor-benzene and dichlor-benzene were used respectively as solvent media. The oil soluble products were recovered

as previously described. The following table illustrates the results obtained:

Solvent	Benzotrichloride	Benzene	Monochlorbenzene	Dichlorbenzene
Structure				
Order of decreasing chemical reactivity of the solvent	→			
Potency of the oil soluble product: Percent required to give a 0° pour in a waxy oil	No potency	No potency	0.1	.06

It will be observed that as the chemical inertness of the solvent medium decreases the potency of the fluid increases and this is dependent upon the structure of the solvent.

Example III

The same ingredients were used in the same proportions as in Example I, except that in the present case 50 parts of a purified kerosene was used as a solvent in one case and an equal volume of tetrachlorethane was used as the solvent in the other. The products were finished in exactly the same manner and various proportions were added to two different oils, each having a pour point of +30° F. The first of these oils, No. 1, was of a type more susceptible to reduction of pour point than No. 2. The comparison of the two products is given in the table below which shows that the product made in the presence of the chlorinated solvent produced a pour depression on an average of 10 to 25° below that produced by an equal quantity of the material made in the presence of the kerosene:

Percent added	Made in kerosene		Made in tetrachlorethane	
	Waxy oil No. 1	Waxy oil No. 2	Waxy oil No. 1	Waxy oil No. 2
.30	−10°	Pour −5° F.	−35	−20
.15	0°	+15	−20	−10
.075	+15	+25	−10	0
.0375	+20	+30	0	+20

Example IV

In the above example the volume of tetrachlorethane was quite large and in no case where the solvent was used was there any oil insoluble product produced. In the present example, the proportion of the ingredients was the same as before except that the amount of solvent was greatly reduced, only 15 parts being used for 100 parts of the chlorinated wax. Furthermore, the temperature of reaction was 125° F. and the reaction time about 2½ hours.

Under the above conditions, when no solvent was used there was a very large production of oil insoluble rubbery material which amounted to approximately 20% of the total reaction product. The yield of the purified inhibitor amounted to 60.5% based on the reactants. Where the chlorinated solvent was used there was a very small amount of insoluble material which was separated without difficulty and a final yield of 71.3% of the depressant was obtained. The depressant in both cases was of about the same strength. This example shows that even a small amount of the particular solvent material will greatly reduce the amount of insoluble reaction product, although there was not quite enough in the present case to completely eliminate the insoluble product.

Example V

The conditions of the present example closely approximated those of the prior example except that 15 parts by volume of ortho dichlorbenzene was used as the solvent, and the reaction period was three hours. No insoluble product was produced where this solvent was employed and the potency was such as to give a pour reduction of 5 to 10° more on the average than could be obtained with an equal amount of product made without the solvent.

Example VI

Two condensations were made with the same ingredients in the same proportions, the difference between the tests being that in the first the catalyst was added to a mixture of chlorwax and naphthalene in the presence of the solvent while in the second the chlorwax was added to the mixture of the naphthalene and catalyst in the presence of the solvent. The ingredients were:

	Parts
Chlorinated wax (13% Cl)	100
Naphthalene	13.5
$AlCl_3$	1.4
Tetrachlorethane (solvent)	43.0

The temperature during the condensation was maintained at 125° F. and the time of reaction was three hours in each case. The finishing procedure was substantially the same in both instances and consisted in neutralizing the reaction mixture with caustic settling the catalyst sludge and reducing with fire and steam to a temperature of 600° F. in order to remove solvent and unreacted waxy material.

At the end of the first experiment it was found that there was an insoluble or gummy material present to the amount of about 20% of the total product, but there was no such material present in the condensation product produced in the second case.

The products of the two experiments were tested in the same waxy oils and it was found that the material made in the second test gave in all cases 5 to 10° F. greater pour reduction than could be obtained with the product of the first test. When these materials were added to a waxy oil having a 30° F. pour point, it was found that .0375% of the product of the first test was required to produce a pour point of .0° F., while only .020% of the second material was required for the same reduction.

Example VII

Paraffin wax (122° M. P.) was chlorinated to a chlorine content of about 15%. The ingredients were:

	Parts
Chlorinated wax (15% Cl)	100
Naphthalene	13.5
$AlCl_3$	1.4
Tetrachlorethane (solvent)	43.0

The naphthalene and $AlCl_3$ were added to the tetrachlorethane and the temperature adjusted to 125° F. The chlorinated wax was then added to the mixture of naphthalene and $AlCl_3$. The temperature was maintained at 125° F. and the reaction time was 3 hours. The finishing procedure was the same as described in Example VI, and consisted in neutralizing the reaction mixture

with caustic settling the catalyst sludge and reducing the clear oil with fire and steam to a temperature of 600° F. in order to remove solvent and unreacted waxy material.

In spite of the high chlorine content of the chlorwax used in this experiment, there was no oil insoluble material formed during the condensation reaction and the finished recovered synthetic product had a Saybolt viscosity of 8,700 seconds at 210° F. The product tested in a waxy oil was of high potency, it was found that .0375% of the product lowered the pour point from +30° F. to −5° F.

The present invention is not limited to any theory of the mechanism of the reaction nor to any reason for the improvements brought about by the use of any particular solvents, nor to any particular solvents, but only to the following claims in which it is desired to claim the invention as broadly as the art permits.

We claim:

1. In a process for producing wax modifiers in which chlorinated paraffin wax and an aromatic compound are condensed by means of aluminum chloride catalyst, the improvement which comprises mixing the aromatic compound and the catalyst with a chlorinated hydrocarbon solvent which is relatively inert under the reaction conditions, then adding a chlorinated wax to the mixture in which the chlorine content is in excess of 11% and effecting the condensation.

2. Process according to claim 1 in which the solvent comprises a polychlorinated aliphatic hydrocarbon of two to three carbon atoms.

3. Process according to claim 1 in which the solvent is a saturated polychlorinated aliphatic hydrocarbon of two to three carbon atoms.

4. Process according to claim 1 in which the solvent is tetrachlor ethane.

5. In a process for producing wax modifiers by condensation of chlorinated paraffin wax and aromatic compounds with catalysts of the Friedel Craft type, the improvements comprising preparing a mixture of the aromatic compound and the catalyst in a saturated polyhalogenated hydrocarbon solvent of two to three carbon atoms, adding thereto chlorinated paraffin wax and maintaining the temperature below 200° F. to effect the reaction, then separating the catalytic material.

6. Process according to claim 5 in which the chlorine content of the wax is above 11%.

7. Process according to claim 5 in which the chlorine content of the wax is above 11% and the solvent comprises a saturated polychlorinated aliphatic hydrocarbon of two to three carbon atoms.

8. Process according to claim 5 in which the solvent is tetrachlor ethane.

9. In a process for producing wax modifiers by condensation of chlorinated paraffin wax and aromatic hydrocarbons by means of aluminum chloride, the improvement comprising preparing a mixture of the aromatic hydrocarbon and aluminum chloride in tetrachlor ethane as a solvent, then adding thereto the chlorinated paraffin wax which has a chlorine content between about 13 to 20% by weight, maintaining the temperature below about 200° F. to effect the reaction, then separating the catalyst and the solvent.

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