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PROCESS FOR PREPARING POUR
DEPRESSANTS

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This invention relates to lubricating oil additive materials. Particularly it relates to the preparation of lubricating oil additives which depress the temperature at which the lubricant loses its property of free flow. More particularly the invention relates to a method for the preparation of alkylated aromatic compounds utilizing a novel technique.

The lubricant art is familiar with the concept of improving the characteristics of lubricating oils by adding to them minor proportions of materials designed to lower the pour point, increase the viscosity index, improve detergency, inhibit oxidation and rust formation, improve the extreme pressure resisting characteristics and the like. It has been found that a technical and economic advantage exists, in some instances, in favor of the use of additives over more stringent and rigorous refinement of the oil. This is particularly true in the case of methods of lowering the pour point of lubricating oil, i. e., of reducing the temperature at which the oil loses its ability to flow freely. This loss in fluidity is caused by the presence of wax crystals which form an interlinking mass at low temperatures, entrapping the oil droplets therein and rendering the lubricant essentially immobile. The obvious method to solve this problem is to remove the wax from the oil. In some cases this is done but it has been found advantageous from an economic and quality standpoint to only partially remove the wax from the oil and to inhibit the formation of any wax crystals remaining in the oil by means of an additive material. It is believed that the additive, known as a pour point depressor, coats the seed crystals of wax formed and prevents their growth and subsequent entrapment of the oil until a very low temperature is reached, say in the neighborhood of -20° or -30° F.

Outstanding pour depressing agents for many types of lubricants are made by the alkylation of aromatic compounds with long chain molecules of a paraffinic type. Materials such as alkylated naphthalene, phenol, and the like are at present commercially available for use as pour point depressants and are extremely effective. It is to the preparation of these alkylated aromatics that this invention particularly relates.

The preparation of the alkylated aromatic pour point depressors is accomplished by condensing certain paraffinic materials with aromatic materials in the presence of a Friedel-Crafts catalyst. While the condensation may be carried out without the use of a solvent, a solvent is definitely advantageous as a means of control over the different variables in the reaction. Furthermore, as

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shown in the prior art, the solvent used has a pronounced effect on the character of the product obtained. For example, it is well known that by using solvents, such as chlorinated aromatics, superior products are obtained over those in which no solvent is used.

In the prior art methods of preparing these alkylated aromatic pour point depressants the following procedure is customarily used.

The reacting vessel is charged with a solvent, usually a chlorinated solvent such as ortho-dichlorobenzene, and the aromatic material is added. The temperature is raised to the desired level and the catalyst added. The alkylating agent is then added over the desired period of time and the temperature of the reaction adjusted as desired and maintained until the reaction is completed. The catalyst is then "killed" with alcohol and aqueous sodium hydroxide. After removal of the aqueous layer containing the spent catalyst, the product is recovered by fire and steam distillation.

The instant invention relates to an improvement over this technique in that a new and hitherto unusual solvent is substituted in the preparation of the condensate.

It has now been found that superior results are obtained when the chlorinated solvent is replaced by a hydrocarbon oil having a viscosity within a range of about 30 to 220 S. U. S. at 210° F., preferably 140 to 200 S. U. S. The advantages of this substitution are quite striking in that this solvent which is cheaper gives a product having superior pour depressing potency and color. Also, the expensive and time consuming solvent recovery system necessary due to the volatility of the chlorinated solvents is eliminated. The new process also eliminates the health hazards due to the toxicity of the chlorinated solvents.

The operable and preferred reactant conditions are set out in detail in the paragraphs following:

THE AROMATIC MATERIAL

The materials to be alkylated according to the concept of this invention may be chosen from a wide variety of aromatic compounds. Especially operable are the following:

I. Unsubstituted aromatics

benzene
naphthalene
diphenyl
phenanthrene
anthracene
pyrene
chrysene

II. Substituted aromatics

(a) Hydrocarbon derivatives

toluene
xylene
indene
 α -methyl naphthalene
 β -methyl naphthalene
acenaphthene
fluorene

(b) Oxygenated derivatives

phenol
cresol
xylenols
 α -naphthol
 β -naphthol

Especially preferred among these operable compounds, and contemplated in the preferred embodiment, is naphthalene.

ALKYLATION AGENT

The alkylating material which may be used according to the inventive concept may also be chosen from a wide range of alkylation agents. These agents include the following:

I. Halo-alkanes

If the halo-alkane chosen consists of a single halo-alkane, it is essential that there be present a substantial number of polyhalogenated molecules. This is to accomplish the desired interlinking or bonding together of the aromatic molecules to obtain a product having the desired molecular weight. It would be theoretically preferred that the polyhalogenated molecules should have a halogen atom on each terminal group of the molecule. Very satisfactory results are obtained, however, when one or two of the halogen groups are secondary groups.

A mixture of halo-alkanes may be used, so long as there are present a substantial number of polyhalogenated molecules to give the desired chain formation.

Especially desirable are those halo-alkanes having from 8 to 30 carbon atoms, preferably in a straight chain, slight branching of the chain being acceptable, however. Operable halides include the normal or iso-octyl halides, the decyl halides, the lauryl halides, the octadecyl halides, etc., used singly or in admixture. The chlorides are preferred in all instances although the corresponding bromides or iodides can be used. Halogen derivatives of substances which consist of a mixture of hydrocarbons such as paraffin wax, petrolatum, or petroleum which is in the form of halogenated hydrocarbon oils, such as naphtha, kerosene, gas oil, lube oil fractions, and the like are operable.

II. Olefins

An olefinic material may be chosen as the alkylation material used in the process of invention. The olefin chosen may be any of the known olefins containing from 8 to 30 carbon atoms, preferably in a straight chain. Olefins derived from the dehydration of alcohol, from the dehydrohalogenation of primary halides, or those olefins derived from the thermal cracking of hydrocarbons are very useful as the alkylation material. Also operable are the olefins derived from hydrocarbon synthesis processes, from the addition of two hydrogen atoms to an acetylenic compound, or those olefins derived from the polymerization of individual or mixed olefins. Mixtures of the various olefins may, of course, be used, as may conjugated or non-conjugated di-

olefins, singly, or in admixture with the mono-olefins.

It is preferred that if an olefin be chosen it be of type I or type II, that is, one in which the olefinic group is located on the terminal carbon atom. However, the unsaturation or olefinic bond, may be located at any point in the chain so long as there is a relatively straight chain of about 8 to about 25 carbon atoms between the double bond and either the next one or the end of the chain.

Especially useful among the olefins disclosed as operable are those obtained from the thermal cracking of wax or petrolatum. These olefins, being known as cracked wax or cracked petrolatum olefins contain a high percentage of normal olefinic molecules having from 14 to 24 carbon atoms in a straight chain.

Of the various alkylating materials disclosed above, there is preferred, and the preferred embodiment contemplates the use of, the chlorinated paraffin waxes containing from about 20 to 30 carbon atoms in a substantially straight chain, which have been chlorinated to a chlorine content of from about 8% to 30% by weight, 14% to 25% being especially preferred.

THE CATALYST

The catalyst used to affect the condensation reaction may be any of the well-known Friedel-Crafts catalysts, added to the reaction mixture in powder form or in the form of a complex with a short chain alkyl halide such as methyl chloride. Among operable catalysts there may be mentioned AlCl_3 , AlBr_3 , AlBr_2Cl , AlClBr_2 , $\text{Al}_2\text{Br}_5\text{Cl}$, ZnCl_2 , BF_3 , and the like with AlCl_3 being preferred and used in the preferred embodiment.

OPERATING CONDITIONS

Depending upon the final product desired and from the starting materials, various operating conditions may be used. It has generally been found, however, that the time of the alkylation reaction according to the improved process may be varied between about 2 to 8 hours, a preferred time of reaction is between 4 and 6 hours.

Operable reaction temperatures are found within the range of from 75 to 300° F., preferably 100 to 175° F.

The proportions of the reacting ingredients may be varied between about 0.3 and 5 mols of the alkylating agent per mol of the aromatic hydrocarbon being alkylated. It is preferred to use, however, between 1 and 3 mols of the alkylating agent per mol of the aromatic.

SOLVENT

As was stated above the gist of the new improved process involves the use of a hydrocarbon oil as a solvent for the reaction. By the use of this oil several advantages are accomplished. A more potent product is obtained, the expensive and time consuming recovery procedure is eliminated; any toxicity resulting from the use of the hitherto advantageous chlorinated solvents is eliminated.

The hydrocarbon oils operable as solvents in this improved process are those hydrocarbon oils having a viscosity within a range of about 30 to 220 S. U. S., at 210° F. Especially preferred and contemplated in the preferred embodiment are those hydrocarbon oils having viscosities within a range of from 140 to 200 S. U. S. at 210° F.

In order to more explicitly define the instant invention the following examples are given:

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EXAMPLE I

Into a 2000 gallon glass lined Pfaudler reactor there was charged 1115 pounds of a Bright Stock from a Panhandle crude having a viscosity at 210° F. of 150 S. U. S. There was then added 600 pounds of naphthalene. The temperature was then adjusted to 90° F. and 115 pounds of aluminum chloride were added. During the addition of the aluminum chloride the temperature rose to 94° F. Over a period of one hour 5076 pounds of chlorinated wax containing 14.5 percent chlorine was added continuously. During the addition of the chlorinated wax the temperature of the reaction was permitted to rise to 116° F.

After the completion of the addition of the chlorinated wax the reaction temperature was raised slowly to 125° F. and maintained at that point for a total time of 4 hours after the chlorowax addition.

Intermediate samples of the reaction product were taken at 2 and 3 hour intervals, and the catalyst was destroyed with alcohol and aqueous sodium hydroxide.

After 4 hours reaction time the total reaction mixture was diluted with 3145 pounds of a mineral oil having a viscosity at 210° F. of 58 S. U. S. The catalyst was then destroyed with isopropyl alcohol and aqueous sodium hydroxide. The catalyst layer was removed and the product recovered by heating to 540° F. with fire and steam.

Samples of the reaction product and the 2 and 3 hour intermediate samples were evaluated for yield ratio figures. The yield ratio is a true measure of the amount of pour depressant obtained. It is defined as the weight of the commercial pour depressant obtained from a unit weight of unchlorinated wax. In addition portions of the samples were diluted to 25% concentration in Varsol and submitted to the standard Robinson color test. This test is described in detail in the "New and Revised Tag Manual For Inspectors of Petroleum," page 57, Test No. 3, "Color of Lubricating Oils by the Tag-Robinson Colorimeter," 26th edition, 1942. Yield ratios and the Robinson color values on commercial strength depressants from these materials are given in Table I below:

Table I

Sample	Robinson Color	Yield Ratio
2 hours.....	9.75	3.4
3 hours.....	8.75	4.9
final (4 hours).....	9.5	5.2

It will be noted that the yield ratio increases with the reaction time and that the Robinson color of 9.5 in the final product is extremely satisfactory, the colors of the chlor-solvent materials being in the neighborhood of 3 to 4.

EXAMPLE II

Since the yield ratio continued to rise from 2 to 4 hours in the experiment given above the second experiment was carried out duplicating the procedures of Example I with the following exceptions:

(1) The temperature was permitted to rise to 130° F. during the chlorowax addition;

(2) The reaction was carried for 6 hours after the chlorowax addition in order to determine the optimum reaction time;

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(3) Intermediate samples were taken after 2, 3, 4, and 5 hours.

The same Robinson color test of a 25% dilution in Varsol and the yield ratios on commercial strength depressants from these samples and the final sample were taken and are set out in Table II below:

Table II

Sample	Robinson Color	Yield Ratio
2.....	5	5.4
3.....	6	5.6
4.....	4.5	5.6
5.....	5.2	6.0
Final (6 hours).....	6.0	4.7

These data show that the yield ratio increases up to about 5 hours after the chlorowax addition and then begins to decrease. This establishes an optimum reaction time of about 3 to 5 hours.

EXAMPLE III

The commercial depressant prepared from the product in Example II above was blended with 2 test oils in varying proportions and submitted to the ASTM pour point determination test to evaluate its pour point depressant potency.

Oil A was an acid treated paraffin distillate (viscosity about 44 S. U. S. at 210° F.), and Oil B was a 50-50 mixture of oil A and Pennsylvania Bright Stock (viscosity about 150 S. U. S. at 210° F.)

Table III

ASTM POUR POINT DETERMINATIONS

Wt. Percent Additive	ASTM Pour Point, ° F.	
	Oil A	Oil B
None.....	+30	+30
0.09.....	+5	+10
0.15.....	0	-10
0.23.....	-10	-10
0.38.....	-20	-20
0.75.....	-30	-25

These data show that the material prepared in accordance with the instant invention have outstanding utility as pour point depressors in that 0.75% of the additive reduced the pour point 60° F. and 55° F. in oils A and B, respectively.

EXAMPLE IV

It has been found that pour point depressing additive materials tend to lose their ability to depress the pour points of lubricating oils when blends containing the additive are subjected to fluctuating temperatures. These additives are said to be unstable or to furnish unstable pour points. A procedure has been defined to test this loss of pour point reducing ability of various lubricant additives and is known as the S. O. D. pour stability test. It is reported in detail on pages 34-44 of the SAE Quarterly Transactions, volume 12, No. 1, (January 1948). In this test the blend containing the additive is cooled rapidly to 15° F., allowed to warm to 34° F., and held at that temperature for 24 hours. The blend is then again warmed to 50° F. and cooled to -20° F. at the rate of 1° F. per hour. The point at which it becomes solid after this temperature cycling is referred to as the stable solid point.

The material of Example II above was submit-

ted in various percentages in a base oil having a viscosity at 210° of 46 S. U. S., an ASTM pour point of +30° F., and a stable solid point of +20° F. These blends were then submitted to the S. O. D. pour stability test and are set out in Table IV below. For purposes of comparison a product prepared by the standard procedure, that is, using as solvent orthodichlorobenzene, was submitted to the same test conditions.

Table IV

S. O. D. POUR STABILITY DATA

Wt. Percent Additive	Stable Solid Point (° F.)
(oil solvent):	
0.14	-4
0.28	-15
0.56	-10
(ortho-dichlorobenzene solvent):	
0.14	+20
0.28	+20
0.56	+20

These data point out the fact that the additive materials prepared in accordance with the instant invention have outstanding stability when subjected to fluctuating temperatures.

EXAMPLE V

In order to show the effect of the amount of solvent on the improved process of this invention Example II was repeated using various proportions of the solvent oil and yield ratios on the final product were calculated. These data are set out in Table V below:

Table V

EFFECT ON VARYING SOLVENT RATIO

Parts by Weight of Solvent per 100 Parts of Chlorowax	Yield Ratio
15	3.9
20	5.3
25	5.9
25	4.4

These data show that whereas high yield ratios are obtained using from 15 to 25 parts of solvent per 100 parts of chlorowax optimum ratios are obtained from about 20 to 25 parts of solvent per 100 parts of chlorinated wax.

EXAMPLE VI

In order to show the operability of various types of hydrocarbon oils and to establish an operable viscosity range runs similar to Example II were made on laboratory scale changing only the type of hydrocarbon oil used. Yield ratios of the final products were obtained. As a basis of comparison the data obtained are set out in Table VI below:

Table VI

SOLVENT OIL

Source	Vis. at 210° F. (S. U. S.)	Viscosity Index	Depressant Yield Ratio
1. La Crude	44	113	2.0
2. Coastal Crude	54	84	2.0
3. Pa. Crude	45	100	2.0
4. Pa. Crude	152	99	2.4
5. Coastal Crude	38	73	2.8
6. La. Crude	33	109	2.8
7. Coastal Crude	43	75	3.2
8. La. Crude	57	103	3.5
9. Coastal Crude	196	75	4.9
10. Panhandle Crude	164	98	4.3
11. Panhandle Crude	150	100	5.0

The above data show that whereas distillates

having a Saybolt Universal viscosity at 210° F. of within the range of from about 30 to about 220 are operable in this invention those distillates having a viscosity within a range of from about 140 to 200 are preferred since they result in the highest yield ratios.

The alkylated aromatics prepared by the improved process of this invention have outstanding utility as pour point depressants when combined with waxy mineral lubricating oils. The amounts of the additive material to be combined with the mineral lubricating oil will vary somewhat depending upon the base stock used and the results desired. It has been found, however, that blends containing from about 0.02 to 10% by weight of the additive materials of this invention have very desirable low pour points. Satisfactory results are also obtainable with from about 0.1% to 5% by weight and this represents the preferred range.

It has been the practice in the art of lubricating oil additive manufacture to prepare oil concentrates of lubricant additives. These concentrates may be more economically transported and handled, the lubricant manufacturer adding the calculated amount of the concentrate to the base oil to prepare the finished product. Thus, oil concentrates of the additives prepared in accordance with the improved process of this invention may contain from about 10% to 80% by weight of the additive material.

The improved pour depressants of this invention may be blended with the base stock containing any of the well known additives incorporated for furnishing desirable characteristics to the base. Such materials as extreme pressure agents, viscosity index improvers, oxidation inhibitors, detergents, de-emulsifiers, sludge forming inhibitors, rust inhibitors, corrosion inhibitors and the like have all been found to be compatible with these improved pour depressants and blends containing any combination of these may be prepared.

To summarize briefly, this invention teaches the process for the formation of alkylated aromatic pour point depressants which constitutes an outstanding improvement over prior art processes. Whereas the prior art teaches the use of a volatile solvent for the condensation reaction, particularly the chlorinated solvent, the instant invention involves the use of a hydrocarbon oil having a viscosity at 210° F. within the range of from about 30 to 220 S. U. S. In addition to the improved products obtained the use of the instant process results in an economic advantage as well as the elimination of any toxicity.

What is claimed is:

1. An improved process for the preparation of alkylated aromatic materials having utility as pour point depressants which comprises alkylation of an aromatic hydrocarbon with a halogenated aliphatic hydrocarbon in the presence of about 15 to about 30 parts by weight based on 100 parts by weight of the halogenated aliphatic hydrocarbon of a hydrocarbon oil having a viscosity at 210° F. of about 140 to 200 S. U. S.

2. An improved process for the preparation of alkylated aromatic materials having utility as pour point depressants which comprises alkylating an aromatic hydrocarbon with a halogenated aliphatic hydrocarbon in the presence of about 20 parts by weight of a hydrocarbon oil having a viscosity at 210° F. of from about 140 to 200 S. U. S.

3. An improved process for the preparation of

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alkylated aromatic materials having the characteristic of depressing the pour point of lubricating oils with which it has been combined which comprises the steps of admixing an aromatic hydrocarbon with a hydrocarbon oil having a viscosity at 210° F. of within a range of from 140 to 200 S. U. S., adding thereto a Friedel-Crafts alkylation catalyst, thereafter adding sufficient of a halogenated aliphatic hydrocarbon having from 8 to 30 carbon atoms in a straight chain so that there is present in the reaction mixture from .3 to 5 mols of the halogenated aliphatic hydrocarbon per mol of the aromatic hydrocarbon, raising the temperature of the reaction to one within a range of from about 100 to 140° F.,

maintaining the said temperature for a period of time from about 2 to 6 hours and recovering therefrom the desired alkylated aromatic material.

4. A process according to claim 3 wherein from 15 to 30 parts by weight of said hydrocarbon oil per 100 parts by weight of alkylation agent is used.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
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2,297,292	Davis et al.	Sept. 29, 1942