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PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in or relating to the Manufacture of Lubricating Oils

We, Arthur Peverall Lowes, of 154, Liverpool Road, Widnes, Lancashire, Douglas Elwood White, of 24, Beaconsfield Crescent, Widnes, Lancashire, both British Subjects, and Imperial Chemical Industries Limited, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention to be as follows:—

This invention relates to improvements in the manufacture of lubricating oils, and more particularly to a method of manufacturing synthetic lubricating oils of low pour point.

It is well known that the pour point of a lubricating oil is affected by the presence in the oil of wax-like hydrocarbons, and there have been many proposals for lowering the pour point of such oils by freeing them from these wax-like bodies. A common method is to add to the oil a solvent which causes precipitation of the wax on cooling, to separate the precipitated wax and then to remove the solvent from the treated oil. It is also known to prepare synthetic lubricating oils by condensing halogenated wax-like hydrocarbons of high molecular weight with aromatic hydrocarbons in the presence of a condensing agent, and it has been proposed to separate the halogenated hydrocarbon into fractions of differing molecular weight prior to the condensation.

We have now found that oily condensation products of reduced pour point can be prepared from chlorinated paraffin wax or a like chlorinated hydrocarbon and benzene or its homologues, by mixing the aromatic hydrocarbon and the halogenated hydrocarbon, cooling the mixture, removing solids precipitated thereby, and subsequently treating the residual liquid mixture with a condensation agent in known manner.

By cooling such mixtures of chlorinated paraffin waxes and aromatic hydrocarbons, any unchlorinated or inadequately chlorinated paraffin wax present in the mixture separates out, and consequently the condensation product ultimately obtained from the residual liquid is freed from constituents which adversely affect its pour point. Moreover, this invention has the advantage over similar prior proposals, that by using as the diluent the hydrocarbon used in the subsequent condensation, separation of unprecipitated halogenated hydrocarbon from its solvent is obviated.

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The partly chlorinated and unchlorinated paraffins which are precipitated on cooling the chlorinated paraffin wax and aromatic hydrocarbon mixture may, after removal of adhering aromatic hydrocarbon by distillation, be returned for chlorination to a higher degree, and for re-use in the process.

Conveniently, the amount of aromatic hydrocarbon which is added to the chlorinated paraffin wax initially is just sufficient to render the cooled mixture sufficiently mobile to filter readily. However, aromatic hydrocarbon in excess of the above requirement may be used, but we prefer not to use more than is normally required in the condensation reaction. By this means the liquid mixture which results after cooling and removal of the unchlorinated and partly chlorinated solid materials may be submitted directly to the condensation reaction or may, if required, have further aromatic hydrocarbon added to it prior to the condensation reaction.

For a given degree of cooling the amount of solid material formed decreases with increase in the degree of chlorination of the original wax-like body, and thus the extent to which the pour point of the final oil is lowered will vary from case to case. For a given chlorinated derivative and a given aromatic hydrocarbon the pour point of the final oil may be modified and controlled by adjusting the amount of aromatic hydrocarbon and/or by regulating the degree of cooling to which the mixture is submitted. Thus the amount of solid which is precipitated on cooling to a given degree decreases as the amount of aromatic hydrocarbon is increased, and the pour point of the final oil is thereby increased. It is preferable to use only the required amount of aromatic

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hydrocarbon to render the viscosity of the cooled solution such that it will filter readily, so that the precipitated solid material may easily be removed; the use of greater quantities results in a final oil of higher pour point and also requires more heat to be abstracted during the cooling process. For given quantities of halogenated paraffinic hydrocarbon and aromatic hydrocarbon, the lower degree of cooling to which the mixture is submitted the greater is the amount of solid material which separates out, and the lower the pour point of the final oil.

We find that for the condensation of a chlorinated paraffin wax containing 26% chlorine with benzene as the aromatic hydrocarbon, a notable lowering of the pour point is produced with as little as 20% (by volume) of benzene when the mixture is cooled to 14° F.

The condensation reaction can be carried out with the aid of the usual Friedel-Craft condensation reagents such as ferric chloride, anhydrous aluminium chloride, boron fluoride, or aluminium, either activated or not, the reagent being gradually added to the mixed reactants at ordinary temperature.

An evolution of hydrochloric acid indicates that the condensation is proceeding, and when this subsides the mixture is heated to ensure completion of the reaction. The product is finally isolated and purified in known manner. The condensation and subsequent steps may, if desired, be carried out in the presence of an excess of the aromatic hydrocarbon according to copending Application No. 31326/35.

The following Examples in which all parts are by weight, are illustrative of the manner in which the invention can be carried out and of the improvement effected thereby.

Example 1.

One part of chlorinated paraffin wax containing 22% chlorine was mixed with 0.32 part of benzene (i.e. 3 vols. of chlorinated paraffin wax to 1 vol. of benzene) and cooled to 23° F. with stirring, when 14.7% of the chlorinated paraffin wax separated out as a solid containing 8.0% chlorine, and was filtered off. A further 1.06 parts benzene were added to the filtrate and the mixture treated with 0.046 part of anhydrous aluminium chloride with vigorous stirring for 6 hours at room temperature. The reaction mixture was then heated for 1 hour at 80° C., cooled, and allowed to stand until separation into two layers was complete. The upper layer product was washed with 10% hydrochloric acid, followed by water washing until neutral, and the benzene finally distilled off under reduced pressure to yield a residue of lubricating oil with a pour point of 41° F. A lubricating oil prepared in the same way but without separation of the lower chlorinated wax had a pour point of 63° F.

Example 2.

1 part of chlorinated paraffin wax containing 22% chlorine was mixed with 0.44 part of benzene and the mixture divided into two equal portions. On cooling one portion to 14° F., 21.5% of the chlorinated wax separated as a solid containing 10% chlorine and was filtered off. After addition of a further 0.47 part benzene to the filtrate, the liquid was then worked up as described in Example 1. The oil so obtained has a pour point of 28° F., whereas the product obtained in an analogous manner from the uncooled portion had a pour point of 63° F.

Example 3.

1 part chlorinated paraffin wax containing 26% chlorine was mixed with 0.22 part of benzene and the mixture divided into two equal portions. On cooling one portion to 14° F., 23% of the chlorinated wax separated out as a solid containing 10% chlorine and was filtered off. After addition of a further 0.54 part of benzene to the filtrate, the liquid was worked up as described in Example 1. The product obtained had a pour point of 21° F., whereas the product obtained in an analogous manner from the uncooled portion had a pour point of 41° F.

Example 4.

1 part of chlorinated paraffin wax containing 13% chlorine was mixed with 2.15 parts of benzene (i.e. 1 vol. of chlorinated paraffin wax to 2 vols. of benzene) and the whole cooled to 28° F. with stirring, when 36.6% of the chlorinated paraffin wax separated out as a solid containing 4.9% chlorine and was filtered off. The liquid was treated with 0.046 part of anhydrous aluminium chloride and stirred vigorously for 6 hours at room temperature. The reaction mixture was then heated for 1 hour at 80° C., cooled, and allowed to stand until separation into two layers was complete. The upper layer was washed with 10% hydrochloric acid, followed by water washing until neutral, and the benzene finally distilled off under reduced pressure to leave a residue of lubricating oil. This oil had a pour point of 26° F. lower than that of an oil made in a precisely similar but without removing any of the chlorinated wax of low chlorine content.

Dated the 15th day of October, 1936.

E. A. BINGEN,
Solicitor for the Applicants.

COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Lubricating Oils

We, ARTHUR PEVERALL LOWES, of 154, Liverpool Road, Widnes, Lancashire, DOUGLAS ELWOOD WHITE, of 24, Beaconsfield Crescent, Widnes, Lancashire, both British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in the manufacture of lubricating oils, and more particularly to a method of manufacturing synthetic lubricating oils of low pour point.

It is well known that the pour point of a lubricating oil is affected by the presence in the oil of wax-like hydrocarbons, and there have been many proposals for lowering the pour point of such oils by freeing them from these wax-like bodies. A common method is to add to the oil a solvent which causes precipitation of the wax on cooling, to separate the precipitated wax and then to remove the solvent from the treated oil.

It is also known to prepare synthetic lubricating oils by condensing halogenated wax-like hydrocarbons of high molecular weight with aromatic hydrocarbons in the presence of a condensing agent, and in Specification No. 417,659 concerning the manufacture of condensation products of paraffin wax hydrocarbons by halogenating them and subjecting the halogenated products to the action of condensing agents either alone or after addition of cyclic hydrocarbons, it has been proposed to separate the initial materials or their halogenation products into at least two different fractions of different mean molecular weight prior to the condensation. One method of performing this was to mix the halogenated product with a diluent, e.g. a cyclic hydrocarbon, and separate out the desired fraction by cooling, the separated fraction being subsequently condensed with naphthalene or other cyclic hydrocarbon.

It has also been proposed in the manufacture of pour point depressors by condensing a chlorinated hydrocarbon with an aromatic hydrocarbon to separate the chlorinated hydrocarbon, e.g. chlorinated paraffin wax into a fraction consisting substantially of a monochlor derivative and a fraction consisting substantially of a dichlor-derivative, and to condense the latter with an aromatic hydrocarbon in the presence of aluminium chloride. Cooling in the presence of a diluent such as naphtha, benzol, toluene, acetone or carbon tetrachloride was stated to be a suitable method of performing the fractionation.

According to the present invention, oily condensation products of reduced pour point are prepared from chlorinated aliphatic hydrocarbons of high molecular weight, such as chlorinated paraffin wax, and benzene or its homologues by first mixing the chlorinated hydrocarbon and the aromatic hydrocarbon in the absence of a condensing agent, cooling the mixture so as to cause the separation of solids, removing the solids and subsequently subjecting the residual liquid to condensation in the presence of a condensation agent such as anhydrous aluminium chloride, if desired after the addition of a further quantity of the aromatic hydrocarbon.

By cooling such mixtures of chlorinated aliphatic hydrocarbon and aromatic hydrocarbon, any unchlorinated or inadequately chlorinated aliphatic hydrocarbon present in the mixture separates out, and consequently the condensation product ultimately obtained from the residual liquid mixture of aromatic hydrocarbon and the more highly chlorinated fraction of the aliphatic hydrocarbon remaining in solution will be free from the constituents which adversely affect its pour point. Moreover the invention has the advantage over prior proposals, that by using as the diluent the hydrocarbon used in the subsequent condensation, the step of removing the diluent from the chlorinated hydrocarbon before the condensation reaction is rendered unnecessary.

The partly chlorinated and unchlorinated paraffins which are precipitated on cooling the mixture may, after removal of adhering aromatic hydrocarbon, e.g. by distillation, be returned for chlorination to a higher degree, and re-used in the process.

For given ratios of the halogenated

aliphatic hydrocarbon to aromatic hydrocarbon, the lower the temperature to which the mixture is submitted, the greater is the amount of solid which separates out and thus the lower the pour point of the final oil, while for a given temperature the amount of solid removed decreases as the chlorine content of the chlorinated body increases; the extent to which the pour point of the final oil is lowered will thus vary according to the degree of chlorination and the extent of cooling. The proportion of the aromatic hydrocarbon will also affect the amount of solid precipitated, the amount decreasing as the proportion of aromatic hydrocarbon increases with a correspondingly smaller effect on the pour point, so that with a large proportion of the aromatic hydrocarbon, a lower temperature is necessary to produce a given reduction in pour point than if a small proportion is used. On the other hand, with too small a proportion of the aromatic hydrocarbon the cooled liquid may be too viscous to enable the suspended solids to be easily separated. Thus, it was found that a mixture of 1 part of benzene and 2 parts of chlorinated paraffin wax containing 22% chlorine and derived from a wax of setting point 55—57° C. could be cooled to about −10° C. and still be filtered, while a mixture of one volume of benzene with three volumes of such a chlorinated wax could only be cooled to about −5° C. if satisfactory filtration of the solids was to be realised. The precise temperatures to which the mixtures can be cooled are to some extent influenced by the rate at which cooling is carried out since this affects the crystal size of the particles which separate, and thus the ease of filtration.

Preferably therefore, we add to the chlorinated hydrocarbon only sufficient aromatic hydrocarbon to render the mixture mobile enough at the temperature to which it is cooled to enable the solids to be filtered off. The remainder of the aromatic hydrocarbon necessary for the condensation is added after the solids have been removed, and the reaction carried out. By this means the minimum of cooling, and thus of energy consumption, is effective for reducing the pour point of the final product. However, the invention is not restricted to this minimum amount, and greater quantities of the aromatic hydrocarbon may be employed if desired, e.g. to modify the extent to which the pour point is lowered by a given degree of cooling. We prefer not to add a greater quantity than is required to react with the chlorinated hydrocarbon when an inert diluent is to be present during the condensation, or not more than about four times this quantity if the condensation is to be carried out in the presence of an excess of the aromatic hydrocarbon. In many cases useful reductions in pour point can be achieved with quantities which are much less than these; for example, we find that in the condensation of a chlorinated paraffin wax containing 26% chlorine with benzene as the aromatic hydrocarbon a notable lowering in the pour point of the oily condensation product is attained with only 20% (by volume) of benzene, when the mixture is cooled to −10° C.

The condensation reaction is carried out in the usual way on the mixture which has been freed from solids; for example, after adding the extra aromatic hydrocarbon and/or diluent the catalyst may be gradually added at ordinary temperatures and when evolution of the gas subsides, the mixture heated to e.g. 50—80° C. to ensure completion of the reaction; the product can then be worked up by decomposing the catalyst with water, filtering, and distilling off the water and the diluent. Many variations of the condensation process and the subsequent recovery steps are known which are applicable in the present instance, but they form no part of the present invention.

A particularly suitable catalyst for the condensation process is anhydrous aluminium chloride, but the invention is not restricted thereto, for other catalysts of the Friedel-Crafts type may be used such as boron fluoride, anhydrous ferric chloride, and aluminium metal, whether activated or not.

Various aliphatic hydrocarbons of high molecular weight may also be used for preparing the chlorinated derivative. By "high molecular weight" we mean a molecular weight, or in the case of many technical products which are mixtures of aliphatic hydrocarbons a mean molecular weight, of over 200. Examples of such bodies are the paraffin waxes, crude shale waxes and the like. They may be chlorinated to a varying extent prior to treatment by our process, with a corresponding variation in the character of the final condensation product. The magnitude of the difference in pour point produced by our process will vary with the degree of chlorination as has been set forth previously, and there will be a minimum to this degree of chlorination below which so much unchlorinated material has to be removed before a sufficient reduction in pour point of the finished oil is obtained, that it is more economical to start with a more highly chlorinated material. Thus in the case of paraffin wax, commercially valuable results are not obtained if the degree of chlorination is less than about 10%. On the other hand, the more highly chlorinated bodies, e.g. chlorinated paraffin wax containing 45% chlorine usually contain a certain proportion of less highly chlorinated material which can be satisfactorily removed by our method. Nevertheless the invention achieves its greatest usefulness in the treatment of materials containing an intermediate proportion of chlorine, e.g. 20—30%.

The following Examples in which all parts are by weight, are illustrative of the manner in which the invention can be carried out and of the improvement effected thereby.

Example 1.

One part of chlorinated paraffin wax containing 22% chlorine and derived from a wax of setting point 55—57° C. was mixed with 0.32 part of benzene (i.e. 3 vols. of chlorinated paraffin wax to 1 vol. of benzene) and cooled to −5° C. with stirring, when 14.7% of the chlorinated paraffin wax separated out as a solid containing 8.0% chlorine, and was filtered off. A further 1.06 parts benzene were added to the filtrate and the mixture treated with 0.046 part of anhydrous aluminium chloride with vigorous stirring for 6 hours at room temperature. The reaction mixture was then heated for 1 hour at 80° C., cooled, and allowed to stand until separation into two layers was complete. The upper layer product was washed with 10% hydrochloric acid, followed by water washing until neutral, and the benzene finally distilled off under reduced pressure to yield a residue of lubricating oil with a pour point of 5° C. A lubricating oil prepared in the same way but without separation of the lower chlorinated wax had a pour point of 17° C.

Example 2.

1 part of chlorinated paraffin wax containing 22% chlorine and derived from a wax of setting point 55—57° C. was mixed with 0.44 part of benzene and the mixture divided into two equal portions. On cooling one portion to −10° C., 21.5% of the chlorinated wax separated as a solid containing 10% chlorine and was filtered off. After addition of a further 0.47 part benzene to the filtrate, the liquid was then worked up as described in Example 1. The oil so obtained had a pour point of −2° C., whereas the product obtained in an analogous manner from the uncooled portion had a pour point of 17° C.

Example 3.

1 part chlorinated paraffin wax containing 26% chlorine and derived from a wax of setting point 55—57° C. was mixed with 0.22 part of benzene and the mixture divided into two equal portions. On cooling one portion to −10° C., 23% of the chlorinated wax separated out as a solid containing 10% chlorine and was filtered off. After addition of a further 0.54 part of benzene to the filtrate, the liquid was worked up as described in Example 1. The product obtained had a pour point of −6° C., whereas the product obtained in an analogous manner from the uncooled portion had a pour point of 5° C.

Example 4.

1 part of chlorinated paraffin wax containing 13% chlorine and derived from a wax setting point 55—57° C. was mixed with 2.15 parts of benzene (i.e. 1 vol. of chlorinated paraffin wax to 2 vols. of benzene) and the whole cooled to −2° C., with stirring when 36.6% of the chlorinated paraffin wax separated out as a solid containing 4.9% chlorine and was filtered off. The liquid was treated with 0.046 part of anhydrous aluminium chloride and stirred vigorously for 6 hours at room temperature. The reaction mixture was then heated for 1 hour at 80° C., cooled, and allowed to stand until separation into two layers was complete. The upper layer was washed with 10% hydrochloric acid, followed by water washing until neutral, and the benzene finally distilled off under reduced pressure to leave a residue of lubricating oil. This oil had a pour point of 14.5° C., lower than that of an oil made in a precisely similar manner but without removing any of the chlorinated wax of low chlorine content.

Example 5.

1 part of a paraffin wax of setting point 43—46° C., chlorinated to 25.4% chlorine content was mixed with 0.44 part of benzene and cooled with stirring to −10° C., 11.3% of the chlorinated wax separated as a solid and was filtered off. 0.44 part of benzene was then added, and the condensation carried out as in Example 1. The pour point of the final oil was −2° C., whereas the pour point of an oil obtained in a similar way from a specimen of the chlorinated wax not treated by our process had a pour point of 12.5° C.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the manufacture of

synthetic lubricating oils by the condensation of chlorinated aliphatic hydrocarbons of high molecular weight, e.g. chlorinated paraffin wax, with benzene or its homologues, which comprises mixing the chlorinated aliphatic hydrocarbon and the aromatic hydrocarbon in the absence of a condensation agent, cooling the mixture to cause the separation of solids, removing the solids so separated and subsequently subjecting the residual liquid to condensation in the presence of a condensation agent e.g. aluminium chloride, if desired after the addition of a further quantity of the aromatic hydrocarbon.

2. Process as claimed in Claim 1 in which the chlorinated aliphatic hydrocarbon employed is a chlorinated paraffin wax having a chlorine content of approximately 20—30%.

3. Process as claimed in Claim 1 or 2 in which the separated solids are chlorinated and re-used in the process.

4. Process for the manufacture of synthetic lubricating oils substantially as hereinbefore described and illustrated with reference to the Examples.

5. Synthetic lubricating oils whenever prepared by the methods claimed in any of the preceding claims.

Dated the 12th day of October, 1937.

E. A. BINGEN,
Solicitor for the Applicants.

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