Oct. 26, 1937. R. E. MANLEY 2,097,127

LUBRICATING OIL AND METHOD OF TREATING SAME

Filed April 23, 1934 3 Sheets-Sheet 1

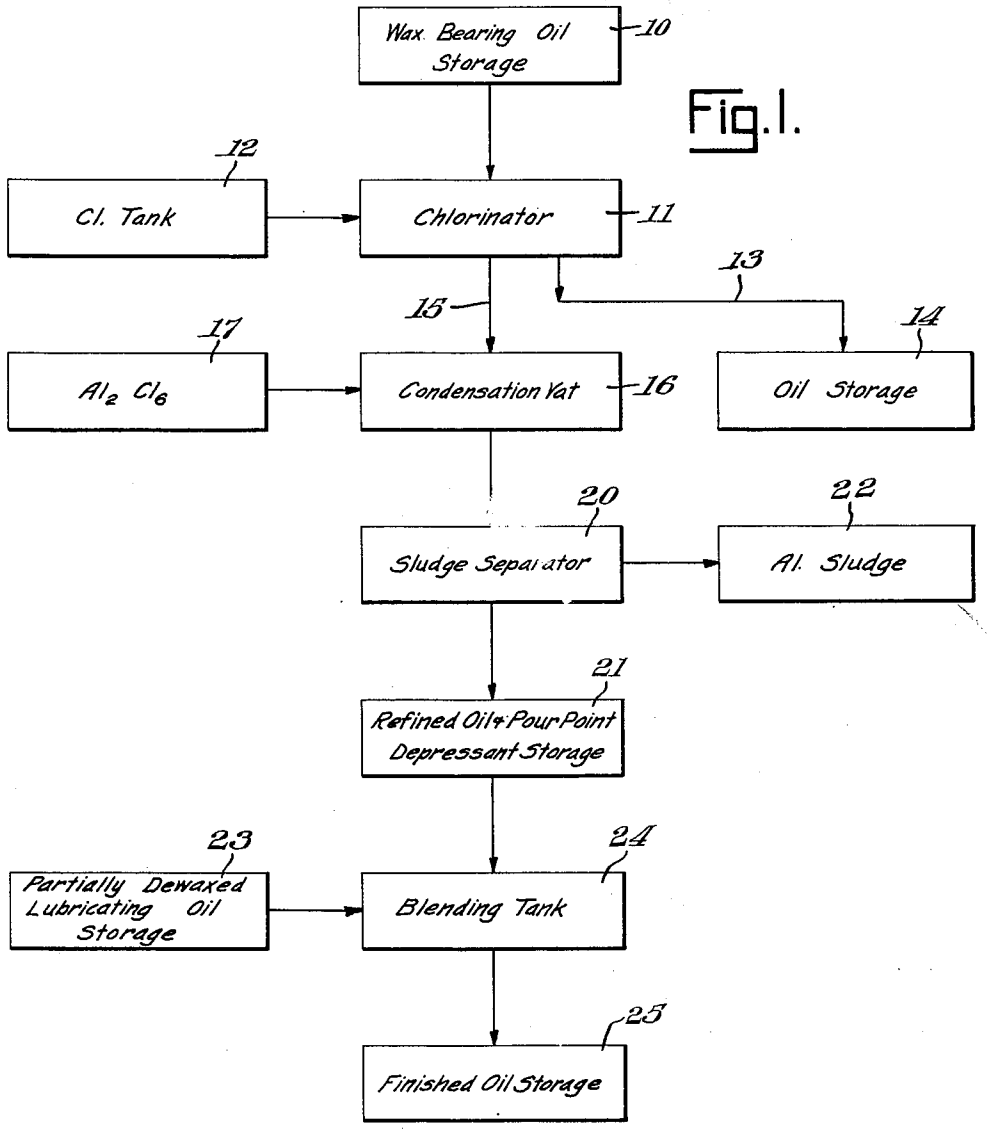


Fig. 1.

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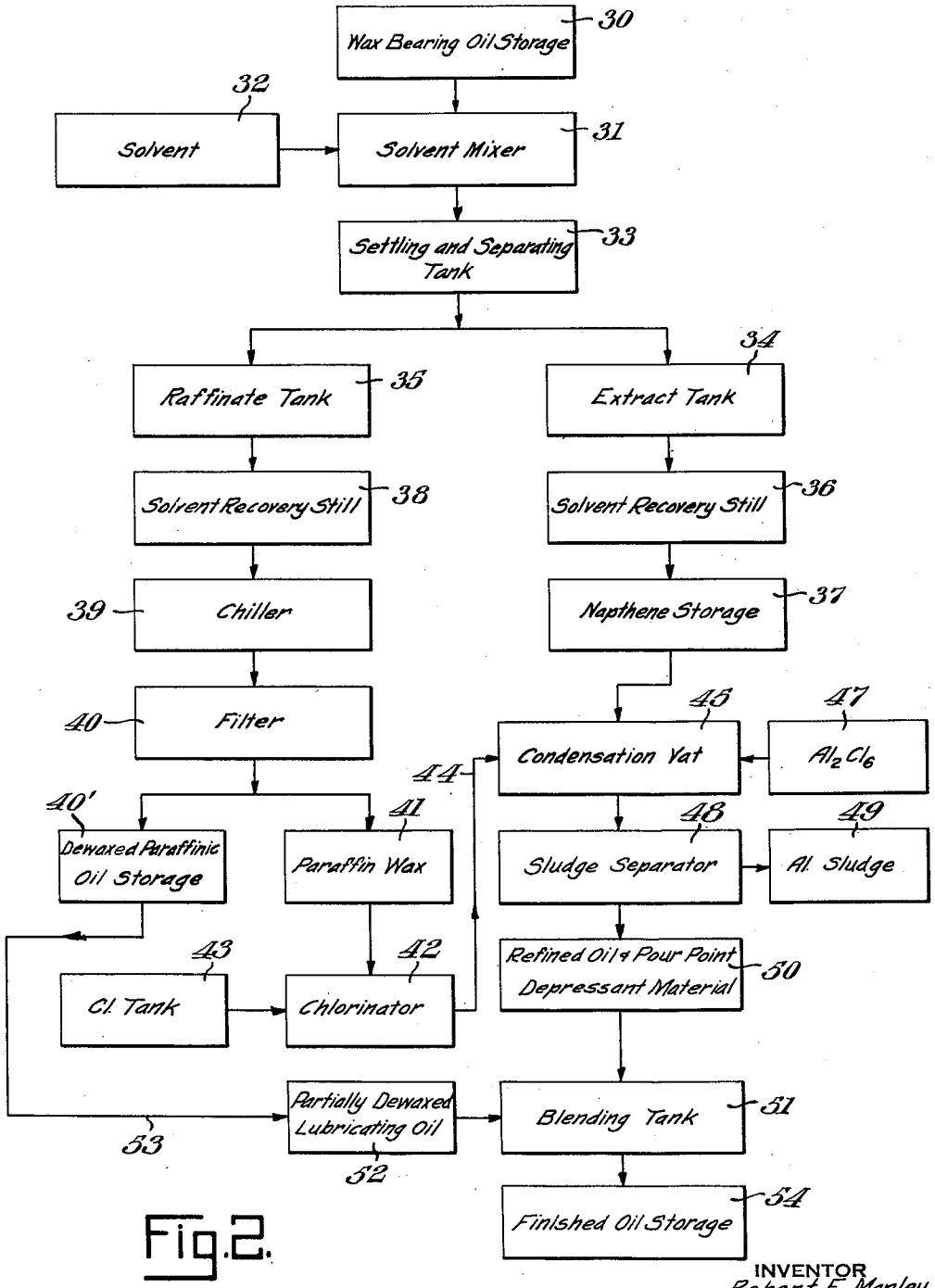


Fig. 2.

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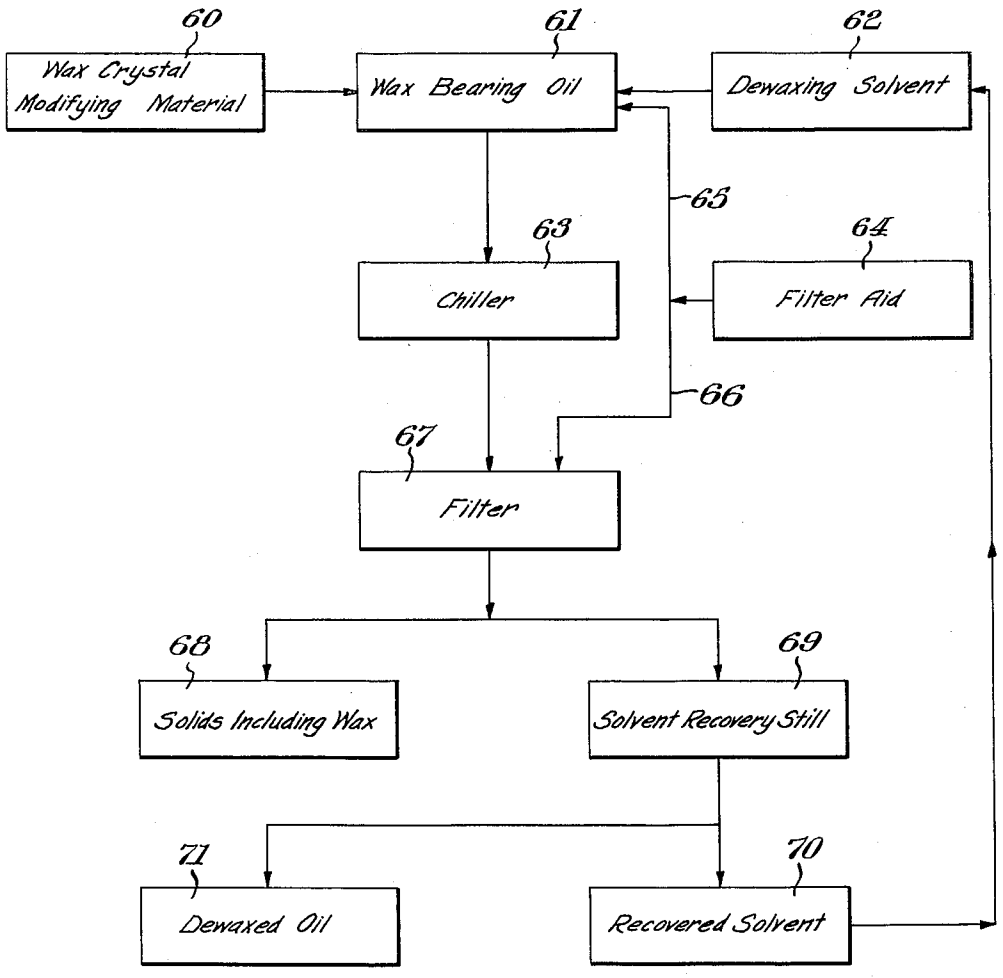


Fig. 3.

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Patented Oct. 26, 1937

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UNITED STATES PATENT OFFICE

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LUBRICATING OIL AND METHOD OF TREATING SAME

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Application April 23, 1934, Serial No. 721,865

5 Claims. (Cl. 196—17)

This invention relates to the manufacture of lubricating oil characterized by a low pour test, and to novel pour point depressants and to methods of producing the same, and to the dewaxing of a wax bearing oil by the employment of such pour point depressants as wax crystal modifying materials.

The invention contemplates the preparation of mineral lubricating oil having a reduced pour test and other desired qualities from lubricating oil stocks, such as those derived from mixed base and paraffin base crudes and the like, by the addition to the lubricating oil of a pour depressing material. The invention particularly contemplates the addition to a lubricating oil of the condensation product in the presence of a Friedel-Craft's catalyst, such as aluminum chloride, of a chlorinated wax bearing lubricating oil, or the condensation product of chlorinated wax and naphthenic constituents of a wax bearing lubricating oil. The invention also contemplates the preparation of a synthetic lubricating oil having a viscosity index and other properties simulating those of a Pennsylvania paraffin base type of lubricating oil containing a proportion of wax, while at the same time the pour point of the synthetic oil is materially below that of a Pennsylvania base wax bearing oil. The invention also contemplates the addition to a wax bearing oil of such condensation products to facilitate dewaxing by filtration, cold settling or centrifuging.

Lubricating oil stock derived from paraffin and mixed base crudes contains appreciable amounts of wax and, therefore, has a relatively high pour test unless a substantial amount of this wax is removed. The removal of this wax is usually accomplished by cold settling, filtration or centrifuging. However, lubricating oil stock, after dewaxing by these processes, may still retain some wax, and may have a pour test well above 0° F., for example, about 25° F. The removal of further quantities of wax from this stock in order to further reduce the pour test necessitates expensive further processing.

On the other hand, the presence of a certain amount of wax in a lubricating oil may be beneficial from the standpoint of providing a comparatively flat temperature-viscosity curve,—that is, a high viscosity index. Consequently, it is of advantage to add to a partially dewaxed lubricating oil a material which will have the effect of reducing the pour test or cold test to the desired extent without the necessity of entirely removing the remaining wax.

It has heretofore been suggested (U. S. patent to Davis No. 1,815,022) that a pour point depressant for a mineral lubricating oil may be prepared by chlorinating paraffin wax or similar straight chain hydrocarbons, and then condensing the chlorinated wax with an aromatic hydrocarbon, such as naphthalene, in the presence of a Friedel-Craft's catalyst. This has heretofore necessitated the selection of comparatively pure or separated organic compounds or products as starting materials; and certain of the aromatic compounds frequently employed may not ordinarily be available at the oil refinery.

It is an object of the present invention to produce a pour point depressant material of this character for a mineral oil directly from a readily available petroleum oil fraction, and which may not require the previous separation or purification of the ingredients entering the reaction to produce the depressant, with resultant material economy.

It is a further object of the invention to provide a synthetic lubricating oil, and a method of producing the same, directly from a wax bearing lubricating oil, which has an unusually low pour test while at the same time possessing a high viscosity index.

Still another object of the invention is to facilitate dewaxing of a wax bearing oil by utilization of the pour point depressants of the present invention to modify wax crystal structure upon chilling of the oil in the presence of such depressants.

Other objects and advantages of the invention will be apparent from the following description and appended claims.

I have discovered that a highly effective pour point depressant material can be prepared from a wax bearing lubricating oil fraction by treating the fraction with chlorine, and then condensing the chlorinated wax bearing fraction in the presence of a Friedel-Craft's catalyst. The resultant oily liquid, when separated from the condensation sludge, is in itself a lubricating oil of low pour test and high viscosity index, and can be employed directly for lubricating purposes. This material, when added to a partially dewaxed lubricating oil in a comparatively small proportion, such as less than 10% by weight and frequently as little as 1% by weight or less, functions as a pour point depressant to materially lower the pour point of the resulting blend. The material, when added in higher proportions, may be used to increase the viscosity index of certain

types of lubricating oil having a comparatively lower viscosity index.

In the accompanying drawings, Fig. 1 is a flow sheet of the method of preparing a synthetic lubricating oil and the pour point depressant material, and of the blended wax bearing lubricating oil having lowered pour point, of the present invention;

Fig. 2 is a flow sheet of a modified procedure of preparing the products of this invention; and

Fig. 3 is a flow sheet of a method of dewaxing, employing the products of the present invention.

Referring to Fig. 1, the wax bearing lubricating oil, which may be a paraffin distillate fraction or a wax bearing residual oil but preferably the former, is passed from a storage tank **10** to a chlorinator **11**. Chlorine gas from pressure tank **12** is passed through the oil in the chlorinator while the oil is preferably heated to a temperature of about 140°–300° F. for a prolonged period. This chlorinated oil may itself be employed as a lubricant, and for this purpose may be passed from the chlorinator **11** by line **13** to oil storage tank **14**.

Preferably, the chlorinated oil is passed for further treatment by the line **15** to the condensation vat **16**. Anhydrous aluminum chloride, which may or may not have been previously dissolved in a light petroleum distillate fraction such as kerosene, is passed from tank **17** to the condensation vat **16**. Controlled streams of the aluminum chloride and the chlorinated oil may be added continuously to the condensation vat, which is equipped with a suitable stirrer, while maintaining an elevated condensation temperature. Any other suitable Friedel-Craft's catalyst, such for example as halides of zinc, iron, antimony, cadmium, boron, manganese, nickel, tin and the like, can be used, although aluminum chloride is preferred. The reaction may be carried out at room temperature, but under such conditions it takes an appreciably longer time.

The reaction mixture is then passed to a separating tank **20**, where the aluminous sludge is allowed to settle. The liquid oil or pour point depressant material is drawn off to storage **21**, and the sludge passed to receiving tank **22**. The refined oil may be subjected to distillation to remove lower boiling hydrocarbon compounds, and thereby improve the flash and fire tests.

The refined oil may be blended with a partially dewaxed lubricating oil from storage tank **23** in the blending tank **24** in wide proportions. Inasmuch as the refined oil is itself a lubricating oil, it may be used directly as such. Where it is desired to reduce the pour point of a partially dewaxed lubricating oil, a proportion of refined oil generally less than 10% by weight is employed, and often as low as 1% or less. The blended oil is then passed to a finished oil storage tank **25**.

As an alternative procedure, the pour point depressant material may be prepared from a wax bearing lubricating oil by first separating naphthenic constituents and wax from the oil, chlorinating the separated wax, and then condensing the chlorinated wax with the separated naphthenic constituents in the presence of a Friedel-Craft's catalyst.

Referring to Fig. 2, in which such an alternative procedure is illustrated, wax bearing oil from storage **30** is passed to a mixing tank **31**, and there mixed with a suitable solvent from tank **32**. Any suitable solvent which is highly selective as between naphthenic and paraffinic constituents of the oil may be employed, such for example as furfural, nitrobenzene, dichlorethyl ether, cresylic acid, liquid sulphur dioxide, etc. Very satisfactory results have been secured employing furfural in the proportions of 3 parts of the solvent to 1 part of oil at a temperature of around 170° F. The solvent mixture is passed to a settling tank **33**, where it is allowed to stratify into layers, from which the extract containing the bulk of the furfural with dissolved naphthenic constituents is removed to an extract tank **34**, and the raffinate containing the bulk of the paraffinic oil and a small proportion of solvent is removed to the raffinate tank **35**. The extract is passed to a solvent recovery still **36**, where the solvent is distilled from the naphthenic constituents and the latter passed to storage **37**. The raffinate is likewise passed to a solvent recovery still **38**; and the solvent free oil then passed through a chiller **39** where the oil is cooled to about 0° F. or below to precipitate the wax. A dewaxing solvent, such as acetone, ethylene dichloride, methyl ethyl ketone, various aliphatic alcohols, and the like, can be employed to facilitate the dewaxing operation. A very satisfactory solvent for this purpose is a mixture of about 35% acetone and 65% benzol for distillate oils, or a mixture of about 28–35% acetone, 47–57% benzol and 15–18% toluol for a residual oil. The chilled mixture is passed to a filter **40**, where the wax is separated from the oil, the latter passing to a dewaxed paraffinic oil storage **40'**. This particular oil is a high grade lubricating oil of high viscosity index, and may be employed as such. Where a dewaxing solvent is not used, or a higher chilling temperature is employed, which results in leaving a proportion of wax in the oil, the latter may be employed as the partially dewaxed lubricating oil with which the pour point depressant is blended.

The paraffin wax is removed from the filter **40** to a receiving tank **41**, from where it is passed to a chlorinator **42** and therein treated with chlorine gas from tank **43** in the manner described above. The chlorinated wax is then passed by line **44** to condensation vat **45** to which the naphthenes are also introduced from storage **37**. The proportions in which the chlorinated wax are mixed with the naphthenic constituents may vary widely, such for example as from 1 part to 10 parts of the chlorinated wax to 1 part of the naphthenes. The condensation of the mixture with a Friedel-Craft's catalyst, such as aluminum chloride, from tank **47**, is carried out in the manner described above. Following the reaction, the sludge is separated in the separator **48** and passed to receiving tank **49**, the refined oil or pour point depressant material being passed to storage **50**. This material is blended in tank **51** with partially dewaxed lubricating oil from storage **52**. A portion of the dewaxed paraffinic oil from storage **40'** may be passed by line **53** to storage tank **52** to serve as lubricating oil to be treated. The finished oil is accumulated in storage **54**.

The products of the present invention are also useful in connection with the removal of wax from a wax bearing hydrocarbon oil. Thus, the addition to a wax bearing oil of a small proportion of the condensation product in the presence of a Friedel-Craft's catalyst of a chlorinated wax bearing lubricating oil, or the condensation product in the presence of a Friedel-Craft's catalyst of naphthenes and chlorinated wax of a wax bearing lubricating oil, is found to modify wax crystal formation upon chilling of the oil, to thereby facilitate separation of the wax from the

oil by centrifuging or cold settling. It is also found that the addition of a wax crystal modifying material of this character to a wax bearing oil results in substantially increasing filtering rates, where the wax is separated from the chilled oil by filtration. The employment of products of the present invention along with a solvent in which both the normally solid and normally liquid constituents of a wax bearing oil are soluble at elevated temperatures of the order of 100° F. or above, and in which the normally liquid constituents are soluble but the normally solid constituents or waxes are substantially completely insoluble at lowered temperatures of the order of 0° F. to −20° F., is found particularly beneficial. Various solvents of this character may be employed, such for example as acetone, ethylene dichloride, methyl ethyl ketone, liquid sulphur dioxide, naphtha, various aliphatic alcohols and the like. Mixtures of a wax solvent and a non-solvent are particularly suitable. For example, a very satisfactory solvent mixture capable of serving as a dewaxing solvent consists of acetone and benzol, for instance in the proportions of 35% acetone and 65% benzol. Another very suitable solvent mixture, particularly for the dewaxing of residual oils, consists of about 28–35% acetone, 47–57% benzol and 15–18% toluol. Very satisfactory results are also secured by adding to the wax bearing oil a comminuted filter aid material of the character of infusorial or diatomaceous earth. This is found beneficial when used in conjunction with the wax crystal modifying material and also with a solvent or solvent mixture.

Referring to Fig. 3 of the drawings, a proportion of wax crystal modifying material of the character described above is added from tank **60** to a wax bearing oil in a suitable mixer or agitator **61**. The proportions in which the modifying material can be added to the wax bearing oil vary; but it is found that by increasing the proportion up to a certain amount for a particular oil gives increasingly beneficial effect, while increasing the proportion beyond that amount gives no further benefit and, in fact, may decrease the effectiveness. For example, a proportion of from 1% to 10% by weight of the condensation products of the present invention, may be used. A dewaxing solvent from storage tank **62** is also preferably added to the wax bearing oil. By way of example, a solvent mixture of 35% acetone and 65% benzol in the proportions of 1 part of oil to 3 parts of acetone-benzol mixture is herein described. The oil mixture is passed through chilling coils **63** where it is chilled to a temperature of around 0° to −10° F. A filter aid material from the hopper feed **64** may be supplied by line **65** to the agitator **61**, so that the oil is chilled in the presence of the filter aid material. Or, the filter aid material can be supplied by line **66** to the already chilled oil as the latter is fed to a filter **67**. Or, a proportion of filter aid can be added both before and after chilling. The filter **67** may be of any suitable conventional construction, such for example as a pressure filter or a continuous filter. The solids including wax are removed by the filter and passed to a receiving vat **68**, while the dewaxed oil and solvent pass to a solvent recovery still **69**. Here, the solvent is distilled from the dewaxed oil, and is passed to a receiving tank **70** from which it may be returned to the storage tank **62** for reuse in the process. The dewaxed oil is accumulated in a receiving tank **71**. Where a solvent mixture of the character of acetone-benzol or acetone-benzol-toluol is employed, the resulting wax free oil is found to have a pour test of around 0° F. when chilled only to about 0° F. or slightly below.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The method of dewaxing a wax bearing oil, which comprises mixing with the wax bearing oil a small proportion of a material selected from the group consisting of a condensation product in the presence of a Friedel-Craft's catalyst of naphthenes and chlorinated wax of a wax bearing lubricating oil, and a condensation product in the presence of a Friedel-Craft's catalyst of a chlorinated wax bearing oil, said material having the property of modifying wax crystal structure upon chilling a wax bearing oil to precipitate wax in the presence thereof, chilling the mixture to precipitate the wax, and separating the wax from the oil.

2. The method of dewaxing a wax bearing oil, which comprises mixing with the oil a solvent selective between the normally liquid and normally solid constituents of the oil and in which the normally liquid constituents are soluble at lowered temperatures while the normally solid constituents are substantially insoluble, together with a material selected from the group consisting of a condensation product in the presence of a Friedel-Craft's catalyst of naphthenes and chlorinated wax of a wax bearing lubricating oil, and a condensation product in the presence of a Friedel-Craft's catalyst of a chlorinated wax bearing oil, said material having the property of modifying wax crystal formation upon chilling of the oil to precipitate wax in the presence thereof, chilling the mixture to precipitate the wax, separating the wax from the oil, and recovering the solvent from the dewaxed oil.

3. The method of dewaxing a wax bearing oil, which comprises mixing with the oil a solvent mixture comprising acetone and benzol, together with a material selected from the group consisting of a condensation product in the presence of a Friedel-Craft's catalyst of naphthenes and chlorinated wax of a wax bearing lubricating oil, and a condensation product in the presence of a Friedel-Craft's catalyst of a chlorinated wax bearing oil, said material having the property of modifying wax crystal formation upon chilling of the oil to precipitate wax in the presence thereof, chilling the mixture to precipitate the wax, and separating the wax from the oil.

4. The method of preparing a lubricating oil having a lowered pour test from a wax-containing lubricant fraction, which comprises solvent refining the lubricant fraction with a solvent which is highly selective as between paraffinic and naphthenic constituents of the oil to separate the oil into a raffinate of increased paraffinicity and an extract of increased naphthenic content, dewaxing the raffinate to remove the bulk of the wax from the oil and produce a partially dewaxed oil normally having a pour test above 0° F., chlorinating wax separated in the above mentioned dewaxing step, condensing the chlorinated wax with extract from the above mentioned solvent refining step in the presence of a Friedel-Craft's catalyst, separating a pour depressant material from the products of condensa-

tion, and adding to the partially dewaxed lubricating oil a minor proportion of the said pour depressant material to produce a resultant lubricating oil having a pour test of about 0° F. or below.

5. The method of preparing lubricating oil having a lowered pour test from a wax-containing lubricant fraction, which comprises solvent refining the lubricant fraction with a selective solvent of the character of furfural to separate a raffinate of increased paraffinicity from an extract of increased naphthenic content, dewaxing the raffinate with a solvent of the character of a ketone-benzol mixture to produce a partially dewaxed lubricating oil normally having a pour test of above 0° F., chlorinating wax separated from the above mentioned dewaxing step, condensing the chlorinated wax with extract from the above mentioned solvent refining step in the presence of a Friedel-Craft's catalyst, separating a pour depressant material from the products of condensation, and adding a minor proportion of the pour depressant material to the partially dewaxed lubricating oil to produce a resultant lubricating oil having a pour test of about 0° F. or below.

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