

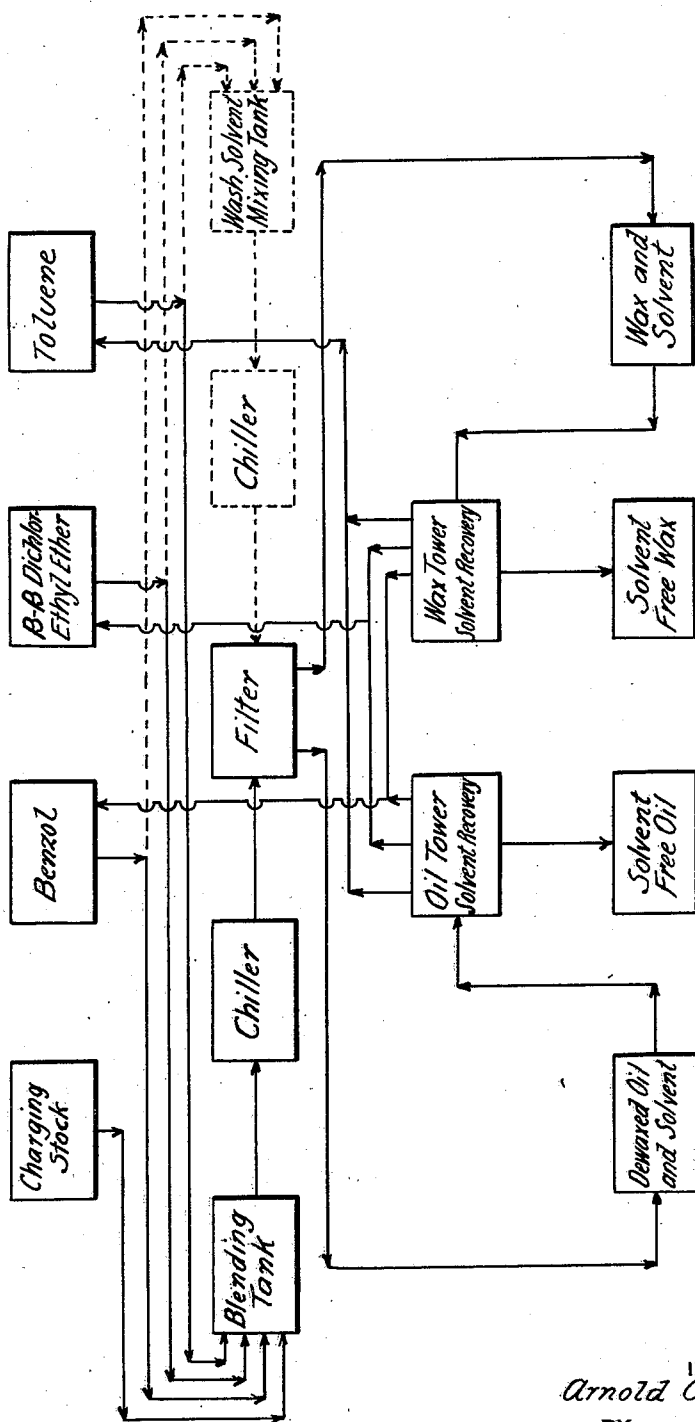
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REFINING OF OIL

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REFINING OF OIL

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This invention relates to improvements in the dewaxing of hydrocarbon oils and more particularly to the dewaxing of petroleum stocks in the manufacture of lubricating oils. The invention provides improved diluent blends which result in increased economy and efficiency of the dewaxing operation.

Heretofore, it has been customary to dewax the stock to be treated by diluting it with a diluent such as petroleum naphtha, chilling this stock mixture to precipitate the wax, and separating the wax from the chilled stock at low temperature. More recently it has been proposed to use liquid propane, methyl acetate, and blends of benzol and acetone, benzol, acetone and toluol, and benzol and methyl acetate as diluents in such dewaxing operations.

The improved diluents of this invention comprise blends of benzol, beta beta dichlorethyl ether, hereinafter generally referred to as ether, and a low freezing point third solvent such as toluene, a mixture of toluol and xylol, or the like, the amount of each of the solvents of the blend lying within definite limits hereinafter more fully described. The improved diluents of this invention have numerous advantages, as will be apparent from the further description.

The diluents of this invention have no detrimental effect on either oil or wax and have a relatively high solvent capacity for oil at low temperatures as well as at higher temperatures. Their high solvent capacity for oil at low temperatures minimizes the retention of oil in the separated wax and thereby promotes a sharp separation between oil and wax.

The diluents of this invention exhibit a ratio of wax solubility to oil solubility which diminishes markedly at low temperatures; that is, the diluents show a marked selectivity for oil over wax at low temperatures such as -20°F. , for example. Cogent evidence of this advantage is observed in the fact that it is not necessary to chill a mixture of the stock and diluents of this invention to an extremely low temperature to yield a product having a noticeably low pour point. For example, it is possible to obtain products of -10°F. pour test from wax-bearing stocks having a viscosity of about 53 seconds at 210°F. by chilling a mixture of the stock and diluents to about -20°F.

The wax precipitated from a mixture of stock and diluent blends of this invention is in condition to be readily separated from the mixture by filtration. The wax is precipitated in a crystallized form and is well adapted to subsequent purification by washing and recrystallization opera-

tions. The diluent blends of this invention, due partly to their high solvent capacity for oil at low temperatures, make it possible to directly precipitate from the stock-diluent mixture a wax of marked purity and high melting point.

The maximum proportion of diluent of this invention normally required to effect dewaxing is about 400 percent by volume calculated upon the volume of stock to be dewaxed although greater amounts may be used with advantage. The large amount of diluent required is more than compensated for by the many advantages which are not obtainable by the use of diluents or diluent blends heretofore known.

The use of diluents of this invention does not demand special and expensive apparatus such as the high pressure apparatus necessary, for example, for use with liquid propane. The boiling range of the diluents of this invention correspond approximately with that of the diluents in conventional use. Accordingly, substantially standard apparatus may be used to recover the diluents of this invention from the products of the dewaxing operation.

The relatively wide boiling range of the diluents of this invention, 176°F. for benzol, 231°F. for toluene, and $284^{\circ}\text{--}297^{\circ}\text{F.}$ for beta beta dichlorethyl ether assist materially in minimizing losses of the diluents. These losses are inherently high for diluents containing benzol together with acetone or methyl acetate, the boiling point of commercial acetone and methyl acetate being $132^{\circ}\text{--}138^{\circ}\text{F.}$ and 135°F. , respectively.

Blends consisting solely of benzol and the ether have been suggested as dewaxing diluents. The use of such diluent blends as previously suggested is open to several serious objections. For instance, there is a tendency of the blends to produce an inferior lubricating oil deficient in body and poor with respect to its viscosity index. Moreover there is a tendency toward the formation of an ether extract phase during the dewaxing operation thus interfering with the recovery of the wax. I have found, however, that within certain definite limits of the proportions of the constituents of the blend, these difficulties are eliminated thus obtaining a superior dewaxing process.

My invention comprises, accordingly, subjecting a wax-bearing petroleum stock to the action of a diluent blend containing benzol and beta beta dichlorethyl ether, the proportion of the ether in the blend lying between approximately 20 and 40 percent of the total volume of the blend, the exact amount of ether depending upon the type of stock

being treated. For example, the ether percentage limitations have been found to be about 25 to 40 percent, based upon the total volume of diluent blend, for treatment of a wax slop comprising an overhead wax distillate stock and about 20 to 30 percent for a heavy bottoms raffinate which has previously been subjected to a nitrobenzene-acid treatment.

I have discovered, furthermore, that when a blend of benzol and the ether is subjected to the low temperatures of the dewaxing operation, say -20°F. , the benzol, because of its relatively high freezing point, separates out, and that such phase separation is prevented without detriment to the operation or the products thereof by adding to the blend definite quantities of a lower freezing, oil-miscible solvent such as toluene, xylol, or the like. A smaller amount of this lower freezing, oil-miscible solvent than the definite quantities hereinafter more fully described does not prevent the separation of benzol. The upper limits of the amount of this lower freezing solvent which may be used are governed by the fact that the wax-yield and pour point of the resulting products are comparatively poorer as the amount of this solvent added tends to displace the benzol in the diluent blend.

My invention further comprises, therefore, subjecting a wax-bearing petroleum stock to the action of the above-described diluent blend which further contains definite quantities of a low freezing, oil-miscible solvent such as toluene, xylol, or the like. The optimum proportion of the lower freezing solvent varies somewhat with the stock being treated. For instance, in dewaxing an overhead wax distillate stock, I have found that the proportion of toluene should not be substantially lower than approximately 10 percent based on the benzol-toluene content of the blend and not substantially lower than approximately 25 percent in dewaxing a heavy bottoms raffinate which has previously been subjected to a nitrobenzene-acid treatment. However, where the benzol used in the blend is of a commercial type containing toluene or similar low freezing constituent as impurities, it will be necessary to add to the blend only sufficient low freezing solvent to bring its total content to the above stated proportions.

The process of my invention may be more clearly understood by a consideration of the accompanying flow diagram. As indicated by the solid lines in the diagram, the charging stock to be dewaxed and the three solvents (beta beta dichlorethyl ether, benzol and toluene) are taken from their respective storage tanks in correct volumetric proportions and pumped into a blending tank which is equipped with means such as a heating coil for raising the temperature of the mixture and means for agitating the mixture. The mixture is therein thoroughly agitated and heated to about 100 to 120°F. after which the warm mixture is pumped through suitable chilling equipment to reduce its temperature to about -10° to -20°F. The chilled mixture is then passed to a suitable filter, and the dewaxed oil-solvent mixture and wax-solvent slurry pass from the filter into their respective run tanks. The dewaxed oil-solvent mixture and wax-solvent slurry are pumped from their respective run tanks to separate solvent recovery distillation units from which the three solvents, stripped from the wax and dewaxed oil, are returned to their respective storage tanks for re-use, thus completing the solvent cycle. The solvent-free

wax and dewaxed oil from the solvent stripping units are finally pumped to their respective run tanks and are then ready for any further treating or finishing operations which may be contemplated.

An additional step may be incorporated in the process for the purpose of more completely washing the oil from the wax cake. When used, the solvent washing step as indicated by the dotted lines on the flow diagram is accomplished by mixing the three solvents (the ether, benzol and toluene) together in a suitable tank in substantially the same proportion in which the solvents were mixed in the primary waxy-oil treatment. The wash solvent mixture is then chilled to substantially the dewaxing temperature used in the primary treatment and forced through the wax cake displacing the oil therefrom. For example, where drum type continuous filters are used the wash solvent mixture may be forced through a perforated spray pipe or series of spray nozzles onto the surface of the wax cake. The mixture of oil and solvent is removed from the filter together with the dewaxed oil-solvent mixture of the primary treatment and pumped into the dewaxed oil run tank for subsequent separation.

It should be understood, however, that the washing of the wax cake on the filter with a cold solvent mixture is not an essential step in the dewaxing process in all cases. For example, where light distillate stocks, which are characterized by large free-filtering wax crystals, are being dewaxed or when large amounts of the solvent mixture are used in the primary dewaxing treatment, that is when 500 to 600% of the solvent mixture is used, the washing step may not be necessary. It is usually desirable, however, to use the solvent washing operation when a wax is being separated from a heavy stock such as heavy wax slops or heavy bottoms raffinates.

The following examples of operation embodying the use of the novel diluents will further illustrate the invention:

Example I

An undewaxed wax slop comprising overhead wax distillate stock having a gravity of 29.2, a viscosity of 53.1 seconds at 210°F. , and a pour test of 100°F. was diluted with 400% of its own volume of a blend of 67.5% benzol, 7.5% toluene, and 25% ether. After chilling to -20°F. and retreatment with 400% of the same diluent blend, a wax yield of 24.3% (based on the stock) was separated from the mixture by filtration. The wax had a gravity of 33.4 and a melting point of 110.7°F. ; the stripped raffinate had a gravity of 27.5, a viscosity index of 92.5, and a pour test of -5°F.

Example II

An undewaxed wax slop comprising overhead wax distillate stock having a gravity of 29.2, a viscosity of 53.1 seconds at 210°F. , and a pour test of 100°F. was diluted with 400% of its own volume of a blend of 54% benzol, 6% toluene, and 40% ether. After chilling to -20°F. and retreatment with 200% of its own volume of the same diluent blend, a wax yield of 26.8% (based on the stock) was separated from the mixture by filtration. The wax had a gravity of 35.0 and a melting point of 109.3°F. ; the stripped raffinate had a gravity of 27.1, a viscosity index of 88.4, and a pour test of -10°F.

Example III

An undewaxed wax slop comprising overhead wax distillate stock having a gravity of 29.2, a viscosity of 53.1 seconds at 210° F., and a pour test of 100° F. was diluted with 400% of its own volume of a blend of 56% benzol, 14% toluene, and 30% ether. Upon chilling to -20° F. and re-treatment with 200% of the same diluent blend, a wax yield of 17.5% (based on the stock) was separated from the mixture by filtration. The wax had a gravity of 35.3 and a melting point of 117.4° F.; the stripped raffinate had a gravity of 27.8, a viscosity index of 88.9, and a pour test of 0° F.

Example IV

A nitrobenzene-acid raffinate comprising a heavy bottoms raffinate having a gravity of 26.4, a viscosity of 171.5 at 210° F., and a pour test of 60° F. was diluted with 400% of its own volume of a blend of 60% benzol, 20% toluene, and 20% ether. After chilling to -20° F. and upon re-treatment with 200% of the same diluent blend, a wax yield of 17.9% (based on the stock) was separated from the mixture by filtration. The wax had a gravity of 28.9 and a melting point of 120.8° F.; the stripped raffinate had a gravity of 26.1, a viscosity index of 103.8, and a pour test of 10° F.

Example V

A nitrobenzene-acid raffinate comprising a heavy bottoms raffinate having a gravity of 26.4, a viscosity of 171.5 at 210° F., and a pour test of 60° F. was diluted with 400% of its own volume of a blend of 52.5% benzol, 17.5% toluene, and 30% ether. After chilling to -20° F. and re-treatment with 200% of the same diluent blend, a wax yield of 20.5% was separated from the mixture by filtration; the wax had a gravity of 27.5 and a melting point of 119.8° F. The stripped raffinate had a gravity of 26.4, a viscosity index of 103.8, and a pour test of 20° F.

Example VI

An undewaxed wax slop comprising overhead wax distillate stock having a gravity of 29.2, a viscosity of 53.1 seconds at 210° F. and a pour test of 100° F., was diluted with 400% of its own volume of a blend of 70% commercial benzol containing approximately 10% toluene, xylol, and the like, and 30% ether. After chilling to -20° F. and re-treatment with 50% of the same diluent blend, a wax yield of 21.1% was separated from the mixture by filtration; the wax had a gravity of 35.6 and a melting point of 123.6° F. The stripped raffinate had a gravity of 27.3, a viscosity index of 88.1, and a pour test of -5° F.

In general, the ether-benzol-toluene dewaxing process is independent of other refining operations to which the oil may be subjected. However, the dewaxing process of my invention may be used in conjunction with a refining operation in which beta beta dichlorethyl ether is the refining solvent. In such a case the raffinate containing a considerable amount of the ether may be subjected directly to the dewaxing process of my invention without intermediate stripping of the refining solvent from the raffinate. The ether content of the raffinate-ether mixture may be readily determined and benzol and toluene may then be added to the raffinate-ether mixture in the blending tank of my process together with any additional amount of the ether which may be necessary to make up the desired ratio of ether-benzol-

toluene in the dewaxing operation. Thus a combined solvent extraction and solvent dewaxing operation may be carried out when using the improved dewaxing solvent blend of my invention.

As used herein, the term "pour test" is the lowest temperature at which the oil will flow when chilled without disturbance, determined, for example, in accordance with method D97-30 of the American Society for Testing Material. Viscosities mentioned herein are viscosities in seconds Saybolt Universal. The percentages of the constituents of the diluent blends set forth in the preceding examples and in the claims are the percentages of the respective constituents with respect to the total volume of diluent blend.

It will be seen, therefore, that my invention comprises an efficient and inexpensive method of dewaxing wax-bearing petroleum stocks by the use of an improved diluent blend whereby a wax of high degree of purity is obtained and an improved petroleum product is obtained which has an advantageous low pour point.

In the specific examples appearing herein I have illustrated my invention as applied to undewaxed wax slop and to a heavy raffinate. It is to be understood, however, that the invention is not limited to the treatment of such stock but contemplates the treatment of any wax-bearing petroleum stock. The specific proportions of the constituents of the blend given in the foregoing examples are those which I have found most suitable to the treatment of the specific stocks selected for the purpose of illustrating my invention and will vary within the specified ranges with the characteristics of the particular wax-bearing stock to be treated, as will be readily understood by one skilled in the art in view of the foregoing examples. Similarly the optimum proportion of the low freezing constituent of the blend for a particular stock will vary somewhat with the temperature to which the mixture is chilled.

I claim:

1. In the solvent dewaxing of a wax-bearing petroleum stock in which the stock and a diluent are chilled to about -20° F., the improvement which comprises separating wax from the stock in the presence of a diluent blend comprising between 25 and 40 percent beta beta dichlorethyl ether and the remainder comprising a mixture of benzol and toluene in which the toluene content of said mixture is not substantially less than about 10 percent.

2. In the solvent dewaxing of a wax-bearing petroleum stock in which the stock and a diluent are chilled to about -20° F., the improvement which comprises separating wax from the stock in the presence of a diluent blend comprising between 20 and 30 percent beta beta dichlorethyl ether and the remainder comprising a mixture of benzol and toluene in which the toluene content of said mixture is not substantially less than about 25 percent.

3. A dewaxing diluent blend for dewaxing a wax-bearing petroleum stock at a chilling temperature of about -20° F. which comprises between 25 and 40 percent beta beta dichlorethyl ether and the remainder comprising a mixture of benzol and toluene in which the toluene content of said mixture is not substantially less than about 10 per cent.

4. A dewaxing diluent blend for dewaxing a wax-bearing petroleum stock at a chilling temperature of about -20° F. which comprises between 20 and 30 percent beta beta dichlorethyl

ether and the remainder comprising a mixture of benzol and toluene in which the toluene content of said mixture is not substantially less than about 25 percent.

- 5 5. In the solvent dewaxing of a wax-bearing petroleum stock in which the stock and a diluent are chilled to about -20°F. with a diluent blend comprising beta beta dichlorethyl ether and benzol wherein the diluent blend has a tendency to separate out into several phases during the dewaxing operation and the stock and diluent blend is chilled to about -20°F. , the improvement which comprises adding to the diluent blend an amount of a low freezing oil-miscible solvent in such an amount as to substantially eliminate the
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separation of phases during the dewaxing operation.

6. In the solvent dewaxing of a wax-bearing petroleum stock in which the stock and a diluent are chilled to about -20°F. with a diluent blend comprising beta beta dichlorethyl ether and benzol wherein the diluent blend has a tendency to separate out into several phases during the dewaxing operation and the stock and diluent blend is chilled to about -20°F. , the improvement which comprises preventing the separation of phases by adding to the diluent blend an amount of toluene not substantially less than about 10%.

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