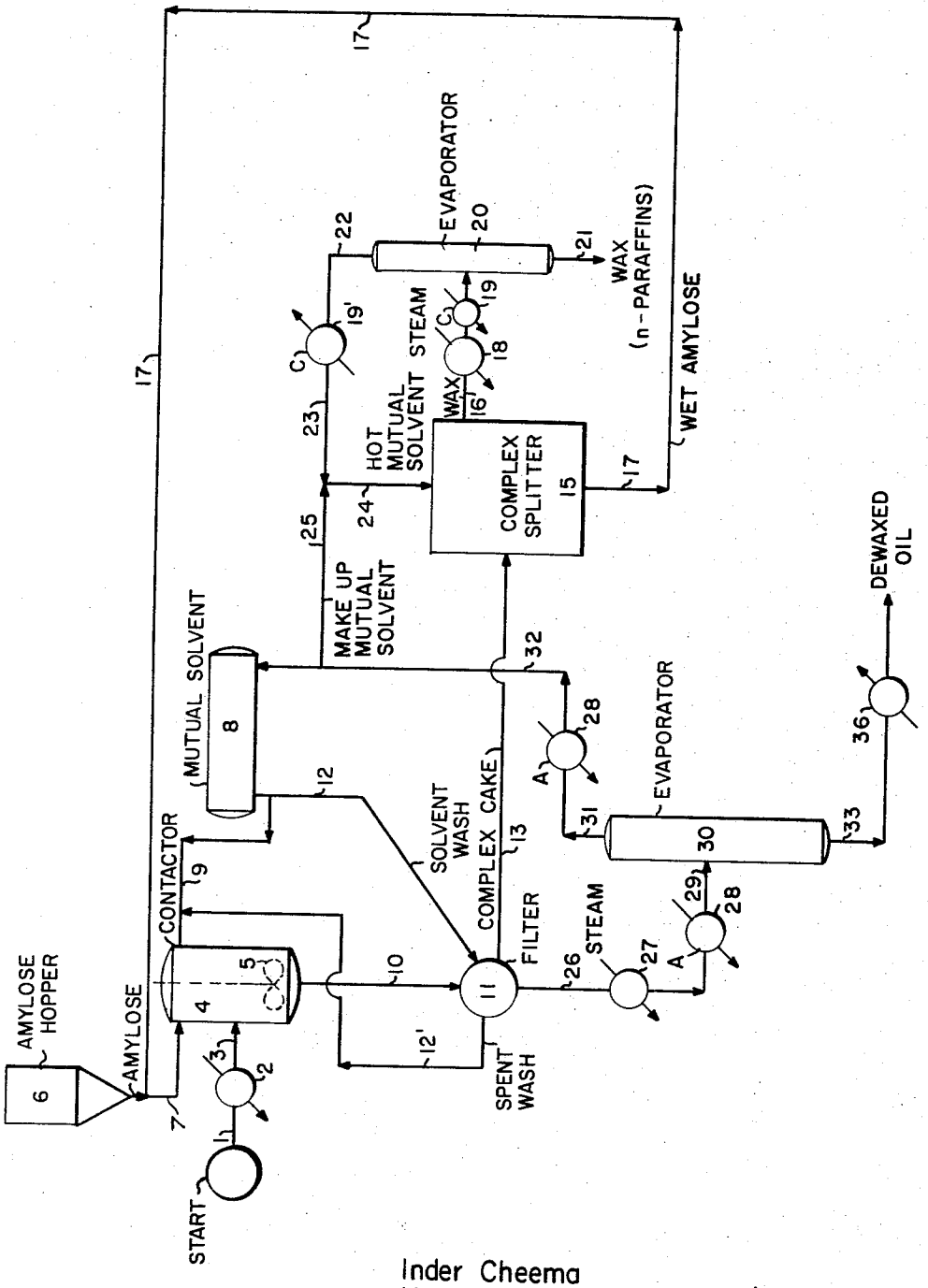
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AMYLOSE IN THE REDUCTION OF POUR POINT

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AMYLOSE IN THE REDUCTION OF POUR POINT

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ABSTRACT OF THE DISCLOSURE

Amylose is utilized to form a complex with normal paraffins in order to remove them from various mixtures. In particular, amylose is used to form a complex with long chain or waxy normal paraffins in order to remove them from a hydrocarbon fraction and thereby lower their pour point.

This invention pertains to an improved method for removing normal paraffins from hydrocarbon mixtures. The normal paraffins may be of any length although they must be capable of forming an inclusion compound. Thus, this invention relates to the removal of normal paraffins from naphthas, kerosene, gas oils and heavier hydrocarbon cuts. With more particularity, this invention pertains to the lowering of the pour point of paraffinic lubes and specialty oils by removing the long chain normal paraffins which contribute to the high pour point. To accomplish this purpose according to this invention, starch amylose is contacted with the normal paraffin containing compound; this starch amylose forms a complex or inclusion compound with the normal paraffins. After the inclusion compound is formed, it can readily be removed by filtration. The invention will be discussed with respect to the dewaxing of paraffinic lubes and specialty oils but it will be readily apparent to one skilled in the art that the same procedure is equally applicable to removing paraffins from other hydrocarbon mixtures such as naphthas, kerosenes and gas oils.

In recent years the demand for low pour point lubricating oils has become extremely high. This is due to a large extent to the greater demand for these oils in regions which experience acute winters. Such regions include Northern United States, Canada, the Scandinavian countries and Switzerland to name just a few. A great variety of lubes and specialty oils must fulfill this requirement of low pour point; typical of these materials are transformer and white oil base stocks as well as motor oils.

This problem is not new although it has increased in the last few years. For decades now a variety of different methods have been used to accomplish the production of a low pour point oil. However, all of them have presented very serious drawbacks which have hindered their use.

Perhaps the two most well-known of these methods are methyl ethyl ketone dewaxing and propane dewaxing.; certainly they are the most widely used dewaxing processes which are capable of getting a pour point down to 0° F.

These processes are successful to some degree however, they are not capable of producing oils with below 0° F. pour points. MEK can give low pour point oils but not economically; further, when using MEK, troubles are encountered while running bright stocks. Propane dewaxing is definitely limited to 0° F. pour points because the lower atmospheric pressure needed for lower chiller temperatures are a distinct safety hazard with propane. This is because any leakage of air into the system would form a combustible mixture with the propane.

As an alternative, the addition of urea to these waxy oils in order to form adducts between the urea and the normal paraffins has also been used to achieve very low pour point lubes. This method, like the other known dewaxing methods, is also extremely expensive. In addition, those who have worked with this method have encountered a substantial problem with corrosion and operability. The nature of urea is such as to cause a good deal of difficulty since it is a highly corrosive material. Liquid urea systems, especially aqueous systems, have exhibited difficulties with emulsions and foams as well as a substantial filtration problem. Urea is also ineffective in producing low pour bright stock.

According to this invention, these problems have now been solved. This invention concerns the addition of starch amylose to a waxy oil solution whereby the starch amylose forms an inclusion compound with the normal paraffins and thereby removes them from the waxy oil solution. The resulting oil has a considerably lower pour point since it is these normal paraffins that contribute to the raising of the pour point.

The starch amylose complex forms when the amylose helix selectively coils around the normal paraffin molecule. The resulting complex can be filtered out of solution and decomposed to regenerate the amylose. After the complex is formed, it is washed for oil removal and then sent to a complex splitter. Here the complex is decomposed into amylose and normal paraffins. Decomposition occurs when temperatures and concentrations are varied so as to destroy the original equilibrium reaction or complex formation. This is done by contacting the complex with hot naphtha, alcohol, water, steam or other well-known complex splitting agents which have previously been heated to the appropriate temperature of 100 to 400° F., preferably 200 to 300° F. The regenerated amylose is recycled while the wax may be sent directly to fuel or otherwise treated to recover complex splitting agents or to permit its use as a product.

In this manner, the great expense associated with the use of urea is eliminated since starch is a far less costly item and amylose may readily be obtained from starch. Furthermore, the difficulties associated with corrosion caused by the urea are also eliminated. Amylose is one of the two major constituents of starch. The other major constituent being amylopectin; of the two major constituents amylopectin is present in a far greater amount. However, amylose may be readily obtained from starch by complexing the amylose out of a dilute dispersed starch solution with butanol. Commercially, there is a process that consists of preparing a molecular dispersion of starch and reacting it in concentrated salt solutions followed by fractionating the amylose and amylopectin at controlled temperatures. Amylose is water-soluble and is primarily responsible for the blue color obtained by the addition of iodine to starch. There is about 4 times as much amylopectin in starch as there is amylose; this will vary with the particular carbohydrates. Amylose is a linear polymer and consists of 200 to 1000 glucopyranose units joined to each other through α1,4-gluosidic linkages. Amylose, when starch is dispersed in water, forms an insoluble complex with butyl alcohol which may be sedimented by centrifugation. The exact amount of amylose within a given starch will vary, starches from so-called waxy grains, as exemplified by waxy corn contains substantially no amylose; whereas starch from certain varieties of peas may contain as much as 75%. The common industrial starches contain roughly 15 to 30% by weight of amylose. There is also now being bred a hybrid corn which would contain 100% amylose, such a product would be especially attractive for the instant invention. About 10 to 70% by weight of amylose is to be added to a mineral oil which is to be dewaxed. Preferably about 10 to 50 wt. percent of amylose is added and most pref-

erably 10 to 30 wt. percent of amylose is introduced into the mineral oil. Among the oils to be treated by this invention are lubricating oils which pour between 60 and 120° F. After treatment with amylose, the oils will pour between −50° and 10° F. Specialty oils, transformer oils and low viscosity blend stocks for 10W and 10W–30 motor oils will have their pour points reduced about 95 to −50° F. by the instant invention.

With respect to conditions, an inclusion compound between amylose and normal paraffins may be formed at a temperature within the range of 0 to 300° F., preferably 70 to 100° F. and most preferably 50 to 80° F. Pressures for the formation of the inclusion compound of the instant invention may vary between 0 and 200 p.s.i.g., preferably 100 and 150 p.s.i.g. An activator or mutual solvent as exemplified by methanol, propanol, isopropyl, alcohol, acetone, ketones and C_1 to C_4 aldehydes may be used to speed up the complexing step. These activators may be utilized in trace amounts. However, these activators are not absolutely necessary and the reaction will proceed for the most part satisfactorily without them.

Contacting times between the amylose and the waxy oil will vary from between 5 to 180 minutes, preferably 5 to 30 minutes and most preferably 5 to 15 minutes. For purposes of this invention a waxy oil may be defined as an oil which contains about 10 to 25 wt. percent of normal paraffins between C_{16} and C_{35}. The amylose may be added in the solid state or may be in solution. If added in solution, about 90 to 95% by weight of water is added along with the amylose.

The resulting solid inclusion compound is separated from the oil solution and is decomposed by heating it at a relatively high temperature or other means such as reaction equilibrium shift via concentration effect. The amylose-waxy complex is separated from the lube oil by simply gravity settling, conventional filtration, centrifugation or other equivalent techniques which are well-known in the art. The complex which is in the form of a filter cake is washed for oil removal and then sent to a complex splitter. Within the splitter, the complex is decomposed into amylose and normal paraffins. Most of the normal paraffins are in the range of C_{16} to C_{35}. As mentioned previously, decomposition occurs when temperatures and concentrations are varied so as to destroy the original equilibrium reaction or complex formation. This may be done by contacting the complex with hot naphtha, alcohol, water, steam or other well-known complex splitting agents which were heated to the needed temperature for complex destruction this temperature would be between 200 and 300° F. The regenerated amylose is then recycled back to the reaction while the wax may be sent directly to fuel or otherwise treated to recover the complex splitting agent if one has been added. The recovered wax may be also used as a product.

The attached figure is a schematic representation of the instant invention.

A waxy oil is introduced through line **1** and passes into heat exchanger **2** where it is raised to a temperature of 100 to 300° F. The waxy oil is removed through line **3** and passes into contactor **4**. This contactor is supplied with agitation means **5**. Solid amylose is stored within amylose hopper **6**. This amylose is easily obtained from commercial firms. The amylose is removed from the bottom of hopper **6** through line **7** and passed into contactor **4**. Contactor **4** is maintained at a temperature of 100 to 300° F. and a pressure of 100 to 200 p.s.i.g. This temperature and pressure is maintained in the initial contacting stage, after which the reacting mixture is cooled in the contactor to ambient temperature so as to facilitate crysallizaion of the complex. As an alternate feature, a *mutual solvent* such as a lower alcohol, ketone such as acetone or C_1 to C_4 aldehyde may be introduced as a promoter. This mutual solvent is stored in storage tank **8** and removed through line **9** from which it is passed into contactor **4**. Amylose, waxy oil (which contains about 10 to 25% of C_{16} or higher normal paraffins) and a mutual solvent activator are contacted with agitation from agitators for a period of about 5 to 60 minutes. At the end of this time, the inclusion compound or complex is formed. About 10 to 50 wt. percent of amylose is added for every weight of waxy oil, about 1 to 5 wt. percent of alcohol is also added per weight of waxy oil.

This treatment results in the removal of about 10 to 25% of the C_{16} plus normal paraffins which are in the waxy oil. Dewaxed lube oil, unreacted starch amylose and the amylose-wax complex pass through line **10** into filter **11** where the wax-amylose complex and unreacted starch is removed as filter cake. Filter **11** may be any conventional filters such as rotary vacuum or pressure or plate and frame. Other means of separation such as centrifugation or simple gravity settling are also possible. Additional mutual solvent may be passed from storage tank **8** through line **12** to serve as a solvent wash during the filtration process. Spent wash is removed through line **12'** and if desired may be recycled back to line **9** to be used as a promoter in complex formation. The complex is removed from filter **11** through line **13** and passed through complex splitter **15**. Within complex splitter **15**, the complex is destroyed by means of heat and diluent which could be naphtha, alcohol, water, steam or some other wel-known compex spitting agent. The temperature within complex splitter **15** is between 100 and 300° F. Hot alcohol is added to the splitter to help effect the separation. The normal paraffin wax is removed from complex splitter **15** through line **16**. Wet amylose is removed from the splitter **15** through line **17** and recycled through line **17** back to line **7** whence it may be used again within contactor **4**. The wax passes through heat exchangers **18** and **19** and finally into evaporator **20**. Purified wax is then removed from the bottom of evaporator **20** through line **21**. These are normal paraffins having a weight of C_{16} to C_{35}. From the top of the evaporator **20**, mutual solvent is removed through line **22** and passes through heat exchanger **19'** wherein the mutual solvent is condensed. From heat exchanger **19'** the mutual solvent is passed through line **23** and then into line **24** where it once again may be passed into splitter **15**. Any additional make-up mutual solvent is introduced into line **24** through line **25**.

Dewaxed oil is removed through line **26**, passed through heat exchanger **27** where the dewaxed oil is approximately 300° F. The dewaxed oil after passing through heat exchanger **27** continues along line **26** from whence it is passed into a second heat exchanger **28'** wherein the dewaxed oil is heat-exchanged with condensing mutual solvent. Following this the dewaxed oil is passed into line **29** where it is transported to evaporator **30**. Mutual solvent, which has served as a promotor, is removed overhead from evaporator **30** through line **31** and sent to condenser **28** where it is condensed. After passing through condenser **28**, the mutual solvent is passed into line **32** where it may return to the mutual solvent storage tank **8** or be further passed through line **25** to be used in the complex splitter. For purposes of this invention, the mutual solvent utilized was 2 propanol, however, other organic promoters may be utilized such as methanol, propanol, C_1 to C_4 aldehydes and ketones. The dewaxed oil is removed from the bottom of evaporator **30** through line **33** and passed into heat exchanger **36**. Finally, dewaxed oil at a temperature of 150 to 175° F. is removed from the heat exchanger **35**. This dewaxed oil has a pour point of −10 to −20° F. which represents an improvement of 20 to 30° F. over the pour point the oil originally had prior to introduction into the system of the instant invention.

This refers to second stage dewaxing. It is anticipated that the same final pour point could be achieved with single stage amylose dewaxing.

Example

In an actual example of the instant invention, a waxy oil which was a Solvent–100 Neutral having a viscosity of 105 SSU at a temperature of 100° F. was contacted with solid starch amylose. About 100 cc. of the waxy oil were contacted with 50 grams of solid starch amylose. The amylose was obtained from commercial sources. The oil contained about 12 grams of wax. About 60 cc. of isopropyl alcohol and 1 volume of heptane diluent per volume of oil were vigorously mixed in a beaker. The complex and unreacted amylose were separated from the diluted oil by filtration. Distillation of the filtrate gave a solvent-free oil for a pour point analysis. The dewaxed oil had a pour point of 65 to 75° F. This indicates a lowering of the pour point by 20 to 30° F. In the beaker, the temperature was maintained at 70 to 140° F. for a period of 30 to 180 minutes, pressure during this time was maintained under ambient conditions.

Although this invention has been described with some degree of particularity, it is intended only to be limited by the attached claims.

What is claimed is:

1. An improved process for lowering the pour point of a waxy oil fraction, the said waxy oil fraction pouring at a temperature of 60 to 120° F. and containing waxy long chain normal paraffins which comprises contacting the said waxy oil fraction with 10–70 wt. percent of amylose whereby a complex forms between said amylose and said long chain normal paraffins, the said contacting taking place at a temperature of 0 to 300° F. and a pressure of 0 to 200 p.s.i.g. for a period of 5 to 180 minutes, filtering the said waxy oil whereby the said complex is removed and a dewaxed oil is obtained which pours at a temperature of —50 to 10° F.

2. The process of claim **1** wherein said complex is passed to a complex splitting zone whereby the complex is subjected to a temperature of 200 to 300° F. and the said complex is broken whereby the amylose is recovered.

3. The process of claim **1** wherein the said long chain normal paraffins have a length of at least C_{16}.

4. The process of claim **1** wherein a solvent activator is added during the said contacting step to facilitate the formation of the said complex.

5. The process of claim **1** wherein the said activator is selected from the group consisting of methanol, propanol, isopropyl alcohol and methyl ethyl ketone, acetone and C_1 to C_4 aldehydes.

6. An improved process for lowering the pour point of a waxy oil solution, the said waxy oil solution containing waxy long chain normal paraffins which comprises contacting said waxy oil solution with 10 to 70 wt. percent of amylose and a solvent activator at a temperature of 0 to 300° F., a pressure of 0 to 200 p.s.i.g. for a period of 5 to 180 minutes whereby a complex is formed between the said amylose and the said paraffins, filtering the said solution to remove the said complex whereby a lower pouring dewaxed oil is obtained, passing said complex to a complex splitting zone, splitting said complex by subjecting it to elevated temperatures within the said splitting zone, removing a separate amylose stream from said complex and a separate stream of long chain normal paraffins.

7. The process of claim **6** wherein the said separate amylose stream is recycled and used in the said contacting step.

8. The process of claim **6** wherein said activator is selected from the group consisting of methanol, propanol, isopropyl alcohol, acetone, ketone and C_1 to C_5 aldehydes.

9. An improved process for lowering the pour point of a waxy oil solution, the said waxy oil solution pouring at a relatively elevated temperature and containing C_{16} through C_{35} long chain normal paraffins which comprises contacting said solution with 10–70 wt. percent of amylose whereby a complex forms between said amylose and said long chain normal paraffins, the said contacting taking place at a temperature of 0° to 300° F. and a pressure of 0 to 200 p.s.i.g. for a period of 5 to 180 minutes, filtering said waxy oil whereby the said complex is removed and obtaining a dewaxed oil with a reduced pour point.

10. The process of claim **1** wherein said waxy oil solution is a lube oil.

11. The process of claim **1** wherein the complex is separated into amylose and paraffin after being filtered by subjecting it to elevated temperatures.

References Cited

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