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DECOLORIZING PETROLEUM WITH AROMATIC SULFONIC ACIDS

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Fig. 1

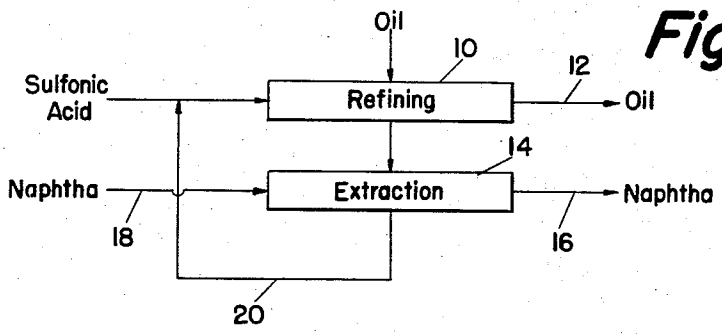
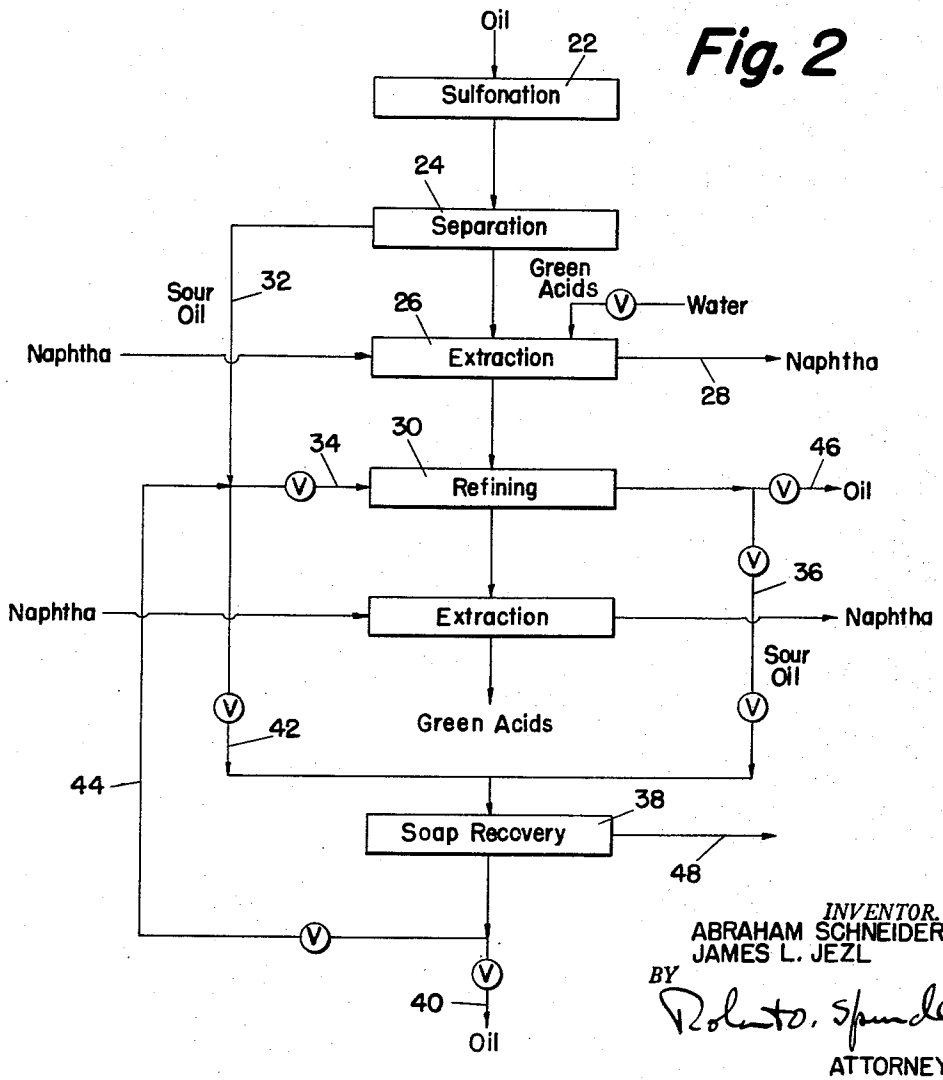


Fig. 2



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DECOLORIZING PETROLEUM WITH AROMATIC SULFONIC ACIDS

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6 Claims. (Cl. 208—282)

This invention relates to the improvement of color of petroleum materials.

The color of petroleum products is frequently an important property thereof, and it often occurs that the products produced by conventional petroleum refining procedures do not have sufficiently good color for the purpose intended. The present invention provides a novel and advantageous manner of improving color by use of a decolorizing agent which is capable of being conditioned for re-use a plurality of times.

In one embodiment, the decolorizing agent is itself produced during petroleum refining operations involving treatment of petroleum oil with a sulfonating agent. In such treatment, oil-insoluble sulfonic acids are generally produced as a result of sulfonation of aromatic hydrocarbons in the petroleum oil. Such oil-insoluble sulfonic acids are, in one embodiment of the invention, employed as decolorizing agents after first removing certain materials therefrom by procedure as described subsequently.

The oil-insoluble sulfonic acids produced as described above can be employed in the decolorizing of petroleum materials generally. In one embodiment, such acids are employed to decolorize the sulfonated oil produced in the same sulfonation process which produced the oil-insoluble sulfonic acids, or in a similar sulfonation process. In this embodiment, the decolorizing operation can be performed either before or after removal from the sulfonated oil of the oil-soluble sulfonic acids produced in the sulfonation. If the decolorizing operation is performed prior to the separation of the oil-soluble sulfonic acids, a redistribution of sulfonic acids between the oil phase and the refining agent phase generally occurs at the same time that color bodies are extracted from the oil by the decolorizing agent.

In its general aspect, the invention involves contacting petroleum with a decolorizing agent comprising aromatic sulfonic acids, the agent having been prepared by extracting color bodies from aromatic sulfonic acids by means of a liquid hydrocarbon solvent. Hydrocarbons including aromatic, aliphatic and cycloaliphatic hydrocarbons, e.g. benzene, xylenes, n-pentane, petroleum naphtha, cyclohexane, etc. can be employed as the solvent. Normally liquid aliphatic hydrocarbons are preferred.

The decolorizing agent employed according to the invention preferably contains 50 volume percent or less, e.g. 10 to 50 volume percent, of water, and 40 to 90 volume percent of aromatic sulfonic acid. The agent may also contain other constituents, such as oil and sulfuric acid in the case where the agent is a green acid phase obtained in sulfonation of petroleum. It is within the scope of the invention to use anhydrous sulfonic acids as decolorizing agent. However, the presence of water is often desirable, especially in low temperature operation, since water promotes fluidity and ease of handling in such operation.

Preferably, the amount of sulfuric acid in the decolorizing agent is not substantially greater than 20 volume percent of the decolorizing agent, and of oil not substantially greater than 25 volume percent. If desired, sulfonic

acids can be recovered by known procedures, separately from sulfuric acid and oil components of green acids. Separation of sulfonic acids from sulfuric acid can be performed by solvent extraction or by any other suitable means. However, such separation is generally unnecessary.

The contacting of decolorizing agent with petroleum to decolorize the latter is preferably performed at a temperature within the approximate range from 50° F. to 300° F., more preferably at least 140° F. The contacting of decolorizing agent with a hydrocarbon solvent to remove color bodies from the decolorizing agent is also preferably performed at a temperature within the approximate range from 50° F. to 300° F., more preferably at least 140° F. Higher temperatures result in reduced viscosity of the materials involved and thus favor ease of handling. Elevated pressure is employed if necessary to maintain the hydrocarbons in liquid phase.

The invention will be further described with reference to the attached drawing wherein Figure 1 is a schematic flowsheet of one embodiment of the process according to the invention, and Figure 2 is a schematic flowsheet of another embodiment of the process.

Referring to Figure 1, a petroleum oil is introduced into refining zone **10** and contacted therein at about 200° F. with benzene sulfonic acid. The petroleum oil may be any normally liquid or solid petroleum fraction, the oil being introduced in any event in liquid phase. Gasoline, fuel oil, lubricating oil, wax, etc. are examples of suitable petroleum materials for refining according to the invention. The relative amounts of the sulfonic acid phase and of oil are preferably within the approximate range from 0.1 to 1 volume of sulfonic acid phase per volume of oil.

The oil and sulfonic acid phases, after intimate contacting, are allowed to separate into layers, the lighter oil layer being withdrawn through line **12**. This oil can be washed with water in order to remove any sulfonic acid remaining in the oil, or subjected to any other suitable finishing operation such as clay treatment, etc.

The sulfonic acid phase is removed from zone **10** and introduced into line **14**, wherein it is contacted with petroleum naphtha. The ratio of naphtha to the acid phase is preferably within the approximate range from 1 to 20 volumes of naphtha per volume of sulfonic acid phase. The materials are intimately contacted and then allowed to separate into layers. The naphtha layer which is withdrawn through line **16** contains color bodies extracted from the acid phase during the contacting. The removed naphtha can be recycled through means not shown and re-introduced into zone **14** through line **18** to contact additional sulfonic acid phase. Prior to such re-introduction, the naphtha can if desired be separated from color bodies contained therein by distilling the naphtha to leave the color bodies in the residue.

The sulfonic acid phase is removed from zone **14** and returned through line **20** to refining zone **10**, wherein it contacts additional oil to decolorize the latter. The operation can be repeated a plurality of times with the sulfonic acid phase being alternately contacted with oil to remove color bodies from the latter and with naphtha to extract color bodies from the sulfonic acid phase.

Referring now to Figure 2, petroleum oil is introduced into zone **22** wherein it is contacted with a sulfonating agent introduced through means not shown. The oil is preferably a lubricating oil having Saybolt Universal viscosity within the approximate range from 80 seconds at 100° F. to 300 seconds at 210° F. Any suitable sulfonating agent can be employed, various sulfonating agents for sulfonation of petroleum being known in the art, e.g. concentrated sulfuric acid, oleum, anhydrous SO_3, chlorosulfonic acid, etc. A preferred sulfonating

agent is a mixture of vaporous anhydrous SO_3 and a carrier gas. A suitable manner of preparing the latter sulfonation agent is disclosed for example in F. E. Anderson United States Patent No. 2,722,543, issued November 1, 1955.

Preferably the oil is contacted with 10 to 30 pounds of SO_3 or equivalent per barrel of oil at a temperature within the approximate range from room temperature to 300° F. Any suitable known charge stock and sulfonating conditions can be employed, however, examples of such charge stocks and conditions being given in C. A. Cohen United States Patent No. 2,413,311, issued December 31, 1946, and M. R. Lipkin and H. E. Reif United States Patent No. 2,680,716, issued June 8, 1954.

The products of sulfonation are introduced into separation zone **24** wherein they are separated into a sulfonated, or "sour," oil phase and an oil-insoluble or "green" sulfonic acid phase. The separation can be performed if desired in the presence of a suitable diluent for the oil, e.g. a hydrocarbon diluent such as n-pentane, petroleum naphtha, etc.

The green acid phase is introduced into extraction zone **26** wherein it is contacted with a solvent for color bodies, such as petroleum naphtha. If necessary water may also be introduced into zone **26** in order to increase the fluidity of the green acids. Such addition of water can be performed at any desired stage of the operation, to produce a water content for example of 10 to 50 volume percent in the green acid phase. Naphtha containing color bodies extracted from the green acids is withdrawn through line **28** and can be recycled to extraction zone **26** through means not shown. Distillation of the naphtha to separate it from color bodies can be performed if desired prior to such recycling. The conditions of contacting in zone **26** are generally similar to those disclosed in connection with the extraction in zone **14** of Figure 1.

The green acids, from which color bodies have been extracted in zone **26**, are introduced into refining zone **30** and contacted therein with petroleum oil. In one embodiment, the latter is oil removed from zone **24** through line **32** and introduced through line **34** into zone **30**. In another embodiment, the oil introduced into zone **30** is produced by a series of operations as described subsequently. The conditions in zone **30** are generally similar to those described in connection with refining zone **10** of Figure 1. The refining is preferably carried out in the absence of a hydrocarbon diluent such as naphtha, since superior removal of the color bodies by means of the aqueous solution of green acids is obtained in the absence of such diluent. Accordingly, in the embodiment where oil is introduced from line **32** into zone **30**, any diluent associated therewith should be first stripped out by means not shown.

In the case where oil is introduced through line **32** into zone **30**, the refined oil is passed through line **36** into soap recovery zone **38**, wherein it is contacted with an alkaline material such as caustic soda introduced through means not shown. Also introduced into zone **38** through means not shown are aqueous isopropanol and naphtha. The aqueous isopropanol selectively dissolves soaps of sulfonic acids formed by reaction of sulfonic acids with the alkaline material. The naphtha selectively dissolves the oil constituents of the material introduced through line **36**.

The naphtha phase containing dissolved oil is withdrawn through line **40**, and naphtha is stripped therefrom by means not shown. The oil product obtained thereby has improved color as a result of the refining in zone **30**.

In another embodiment, the sour oil withdrawn from zone **24** is passed through lines **32** and **42** into soap recovery zone **38**. A naphtha solution of oil is withdrawn through line **44**, and naphtha is preferably stripped therefrom by means not shown. The oil is then introduced through line **34** into refining zone **30**, wherein it is contacted with green acids in a manner similar to that described previously. In this embodiment, the refined oil is withdrawn through line **46** and can be washed with water or given other suitable finishing treatment.

In either embodiment as described above, the aqueous phase containing dissolved sodium sulfonates is withdrawn from zone **38** through line **48**. The sulfonic acids can be recovered from the aqueous phase by suitable procedure as known in the art, and the recovered alcohol recycled to zone **38** in a conventional manner.

The embodiment wherein oil-soluble sulfonic acids are removed from the sour oil prior to the decolorizing is preferred in that the oil product removed through line **46** in that embodiment generally has somewhat better color than an oil produced according to the other embodiment and removed through line **40**.

It is within the scope of the invention to employ the green acids removed from zone **26** to decolorize any petroleum oil in a manner generally similar to that described in connection with Figure 1. Green acids produced in sulfonation of petroleum fractions are generally preferred for use as decolorizing agents according to the invention. However aromatic sulfonic acids from any source can be employed. Examples of suitable sulfonic acids which can be employed are benzene sulfonic acid, toluene sulfonic acids, xylene sulfonic acids, naphthalene sulfonic acids, etc.

The following examples illustrate the invention:

Example I

100 volumes of a straight run lubricating oil distillate from mixed base crude, the distillate having Saybolt Universal viscosity at 100° F. of 100 seconds and at 210° F. of about 30 seconds, are contacted at 200° F. with 20 volumes of a treating agent containing 80 volume percent of benzene sulfonic acid and 20 volume percent of water. The layers are separated to recover a distillate having improved color.

The sulfonic acid phase containing extracted color bodies is admixed with 400 volumes of n-hexane per 100 volumes of the acid phase. The layers are separated to recover a sulfonic acid phase from which color bodies have been extracted by hexane.

The sulfonic acid phase is used to contact additional distillate as described. The extent of color improvement is approximately the same as in the first treatment. By way of contrast, in re-using the sulfonic acid phase containing extracted color bodies to contact additional distillate as described, without intervening treatment with hexane, less color improvement is obtained than in the case where such intervening treatment has been performed.

Example II

A charge stock as described in Example I is contacted with 20 pounds per barrel of vaporous anhydrous SO_3 at a temperature increasing from atmospheric temperature to about 180° F. during the contacting. The sulfonating agent contains about 20 volume percent of SO_3 and 80 volume percent of air. The products are separated in the absence of added diluent at about 170° F. into an oil-insoluble sulfonic acid phase and an oil phase containing dissolved oil-soluble sulfonic acids.

The oil-insoluble sulfonic acid phase, which contains about 60 parts of sulfonic acids, 20 parts of oil, 15 parts of sulfuric acid and 3 parts of water, is admixed at ambient temperature with about 10 volumes of water and 400 volumes of petroleum naphtha per 100 volumes of oil-insoluble acid phase. The layers are separated to recover a sulfonic acid phase and a naphtha phase containing color bodies.

The oil containing oil-soluble sulfonic acids is neutralized with sodium hydroxide and the resulting sodium sulfonates extracted from the oil with aqueous isopropanol. This is a conventional procedure for recovering oil-soluble sulfonic acids from sour oil.

The resulting oil is contacted at ambient temperature with the sulfonic acid phase obtained in the previous contacting of oil-insoluble acids with naphtha and water. The volume ratio of sulfonic acid phase to oil is about 20:100. The layers are separated to recover an oil having superior color to that of the oil prior to the last-described contacting.

The sulfonic acid layer from the last-described separation contains color bodies extracted from the oil. It is admixed at ambient temperature and pressure with 400 volumes of petroleum naphtha per 100 volumes of the acid phase. The layers are separated to recover an acid phase from which color bodies have been extracted by naphtha. The resulting acids can be re-used as decolorizing agent or used in any of the known ways for using oil-insoluble sulfonic acids.

In another embodiment, the contacting of the sour oil with the oil-insoluble sulfonic acids is performed prior to extraction of the oil-soluble sulfonic acids from the sour oil, the procedure being otherwise similar to that previously described.

The invention claimed is:

1. Process for refining petroleum which comprises: contacting unsulfonated petroleum in liquid phase with an aromatic sulfonic acid, thereby to extract color bodies from the petroleum; separating the sulfonic acid phase from liquid petroleum; contacting the resulting sulfonic acid phase with an added hydrocarbon solvent for said color bodies, thereby to extract the color bodies from the sulfonic acid; and contacting the resulting sulfonic acid phase with additional petroleum, thereby to extract color bodies therefrom.

2. Process according to claim 1 wherein said aromatic sulfonic acid contains 10 to 50 volume percent of water.

3. Process according to claim 1 wherein the temperature of the first-named contacting is in the approximate range from 140 to 300° F.

4. In a process for producing oil-soluble sulfonic acids and refined petroleum hydrocarbons by sulfonating petroleum oil, separating oil-insoluble sulfonic acids from the sulfonated oil, and extracting soaps of oil-soluble sulfonic acids from the sulfonated oil by means of an aqueous alcohol solvent, the improvement which comprises: contacting the resulting oil, from which oil-soluble sulfonic acids have been removed, in liquid phase with an aromatic sulfonic acid, thereby to extract residual color bodies from the oil.

5. Process according to claim 4 wherein said aromatic sulfonic acid comprises oil-insoluble sulfonic acids produced by sulfonation of petroleum, from which acids color bodies have previously been extracted by means of a hydrocarbon solvent.

6. Process according to claim 4 wherein 10 to 100 volumes of said sulfonic acid are employed per 100 volumes of said petroleum.

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