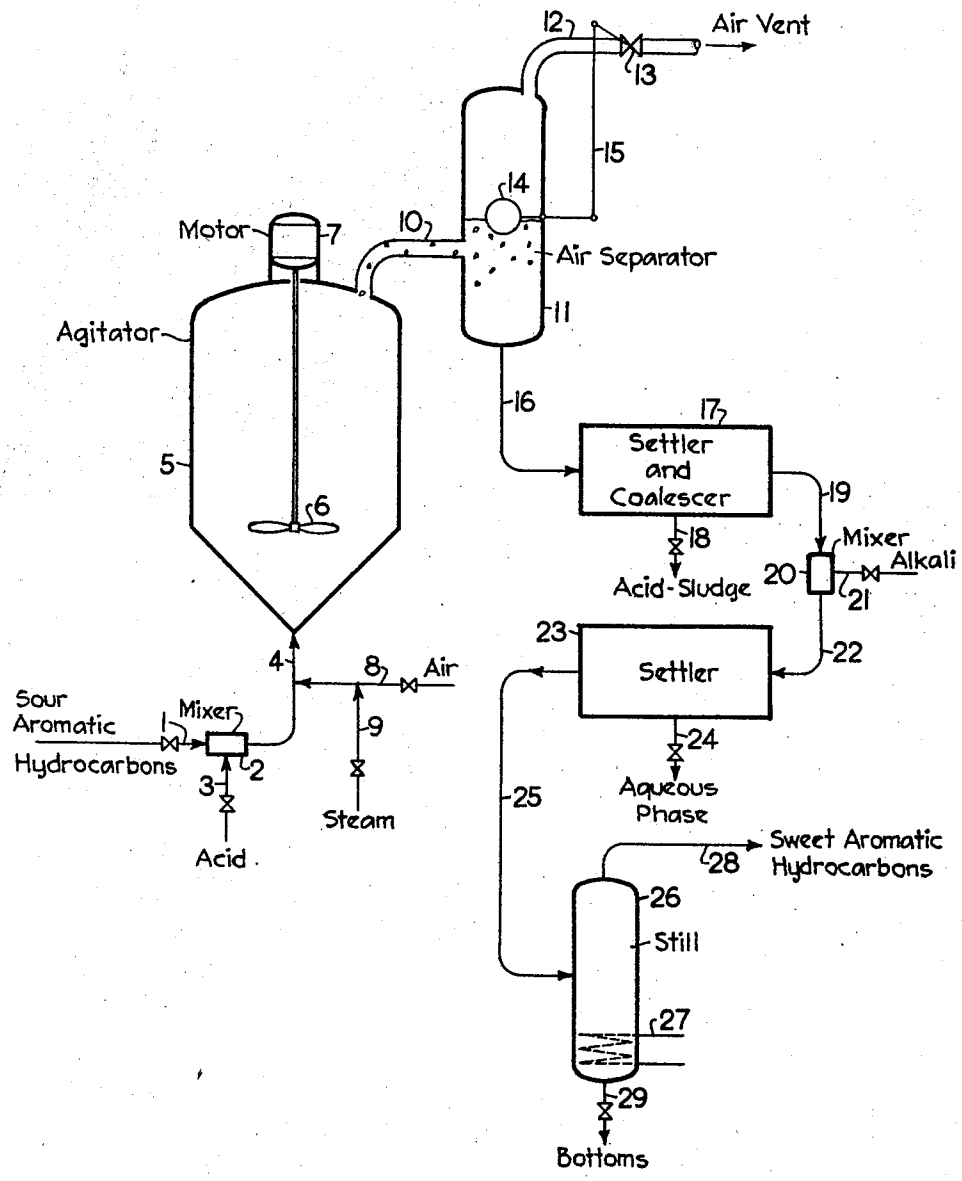
Aug. 29, 1944. G. F. DE RIDDER 2,356,980

TOLUENE SWEETENING

Filed Sept. 21, 1943



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Patented Aug. 29, 1944

2,356,980

UNITED STATES PATENT OFFICE

2,356,980

TOLUENE SWEETENING

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Application September 21, 1943, Serial No. 503,285

11 Claims. (Cl. 196—29)

This invention is concerned with the sweetening of relatively low boiling aromatic hydrocarbons recovered from petroleum distillates with the aid of selective solvents, particularly from naphthas.

For many years the recovery of relatively pure low boiling aromatic hydrocarbons, specifically benzene, toluene, xylenes, ethyl benzene, etc., from petroleum oil has been considered impracticable on a commercial scale, and only in recent years methods have been developed which have made such recovery feasible. Most of these methods employ selective solvents one way or another. Depending upon circumstances, liquid-liquid solvent extraction may be employed, or vapor-liquid extraction (better known as extractive distillation), or azeotropical distillation.

Many different types of solvents may be employed in the separation. For example, liquid SO_2 is suitable for liquid-liquid extraction, as well as most of the selective solvents which have in the past been employed for extracting kerosene or lubricating oils, as for example phenol, cresols, nitrobenzene, nitrotoluene, benzaldehyde, aniline, furfural, beta beta' dichlor diethyl ether, crotonaldehyde, various sulfolanes as sulfolane, methyl sulfolane, dimethyl sulfolane, methyl sulfolanyl ether, etc., and many others. Solvents suitable for extractive distillation have been described in Dunn, U. S. 2,288,126. In azeotropical distillation, one may employ methyl alcohol, ethyl alcohol, acetone, methyl ethyl ketone, acetonitrile, propionitrile, nitromethane, nitroethane, SO_2, ammonia, methylamine, ethylamine, propylamine, etc.

The petroleum naphthas which yield aromatic hydrocarbons may be straight run or cracked or re-formed (both catalytically and non-catalytically), iso-formed, dehydrogenated, isomerized and dehydrogenated, etc., distillates. Depending on the procedure employed, naphtha prior to the separation of the aromatics may or may not contain mercaptans. The present invention is concerned with the treatment of aromatic hydrocarbons recovered by extraction from naphthas which do not contain mercaptans, more particularly aromatic hydrocarbons having between 6 and 10 carbon atoms per molecule and boiling below about 400° F., such as benzene, toluene, xylenes, ethylbenzene, hemimellitene, pseudocumene, mesitylene, etc.

In the separation of aromatic hydrocarbons from some naphthas with the aid of a selective solvent, mercaptans accumulate in the aromatic extract fraction. As a result, the aromatics recovered by these methods, while otherwise of high purity, contain in many instances relatively large amounts of mercaptans. There are many methods known for refining hydrocarbon oils for the purpose of removing mercaptans, outstanding among them being the old sulfuric acid treatment and re-distillation. Sulfuric acid apparently may act in a dual capacity of an oxident and selective solvent, dissolving some mercaptans and converting others to relatively high boiling disulfides, which may then be separated by fractional distillation, provided the naphtha has a relatively narrow boiling range. Its drawback, however, is that it may fail to sweeten completely where mercaptan concentration is relatively high. When attempting to sweeten sour hydrocarbons such as benzene, toluene, etc., it was found that, as a rule, ordinary sulfuric acid treatment and re-distillation, whether carried out in batch or in continuous treating equipment, would not result in complete sweetening. In all these cases it was possible, however, to sweeten successfully when blowing during acid treatment with a large amount of air, the only difficulty being in this case that the amount of air required was so large that serious vaporization losses of the aromatic hydrocarbon occurred. In an effort to overcome losses by vaporization, mechanical agitation alone was tried in an attempt to whip air into the mixture. This was also found to be inadequate in that not enough air could be whipped into the hydrocarbon to completely oxidize the undesirable ingredients and to produce a sufficiently sweet product unless excessively long agitation was employed, which made the process impractical.

The purpose of this invention is to economically, effectively and substantially completely sweeten sour aromatic light hydrocarbon distillates recovered by solvent extraction of naphthas. Another purpose is to reduce the harmful mercaptan content in such aromatic hydrocarbons. A specific purpose is to sweeten sour 1° toluene recovered by extraction of petroleum distillates to produce nitration grade toluene. Other purposes will appear in the following description.

Now it has been discovered that sweetening of sour, relatively low boiling aromatic hydrocarbons can be achieved quite easily and without substantial loss of the valuable hydrocarbon by sulfuric acid treatment and re-distillation, if the sulfuric acid is thoroughly distributed throughout the hydrocarbon liquid by mechanical means and simultaneously a small controlled amount of air is suspended in the liquid together with the acid. This amount of air is substantially less than the

stoichiometrical amount required to convert all of the mercaptans in the oil to disulfides, and preferably is between about ⅛ and ½ of said stoichiometrical amount. If less than this amount of air is employed the hydrocarbons will not be sufficiently sweetened, and if a greater amount of air is employed unnecessary hydrocarbon losses will occur. The air together with the sulfuric acid serves to oxidize the last trace of mercaptans not extracted by the sulfuric acid. In addition to reducing losses by vaporization this procedure has the advantage of always producing a sweet product, and in cases where sweetening with acid alone was possible, of requiring only about half as much acid as is necessary to sweeten in the absence of air. The intensity of mixing the above-mentioned limited amount of air, with the acid, and hydrocarbons must be at least such that during the entire contact time, which usually lasts from about ⅓ up to 10 hours, the air and acid remain suspended in the hydrocarbon liquid. In continuous treating equipment, contact times below about 8 hours are usually sufficient, while in batch treatment, owing to the greater difficulty of thoroughly distributing the air through a large volume of the hydrocarbon liquid, longer contact times are necessary as a rule.

Generally the steps in carrying out the process of this invention comprise: mechanically agitating the hydrocarbon with acid and air; separating the air from the acid and hydrocarbon; and, separating the acid from the hydrocarbon. In order to remove products of oxidation, sulfonation, etc., it is generally necessary to include the additional steps of: neutralizing the hydrocarbon; and, re-distilling the neutralized product.

The accompanying drawing shoes a preferred flow diagram of the process of this invention.

Referring to the drawing, the sour aromatic hydrocarbons are introduced through valved line 1 into the mixer 2, wherein they are contacted with acid introduced through valved line 3. The resulting mixture is then passed through line 4, into a turbo-mixer or agitator 5, provided with an efficient stirrer 6, such as a lightning mixer, driven by a suitable means such as a motor 7. A controlled amount of air is introduced into the agitator through valved line 8, joining line 4. Steam may also be introduced together with this air through valved line 9 to help to keep the temperature of the mixture above about 75° F., and preferably above 85° F. and below about 160° F., as well as to prevent clogging of the openings in line 4. Optimum treating temperature range is between about 110° F. and 120° F. Clogging may be caused by the formation of crystals of aromatic-sulfonic acids. For example, at a temperature of about 75° F., toluene and sulfuric acid react to form toluene-sulfonic acid which readily crystallizes out of solution. At higher temperatures, however, they remain in solution.

In the agitator 5, the air, acid, and sour aromatic hydrocarbons are intensively mixed so that a suspension is produced of sufficient stability to prevent air separation in the agitator and to cause retention in the suspension of a major portion of the air while the latter remains in the agitator. The residence time in the agitator is between about ⅓ to 3 hours. As a result substantially all the mercaptans in the hydrocarbons will either be extracted or oxidized.

This suspension of hydrocarbon, acid, and air passes from the top of the agitator 5, through line 10, into air separator 11, provided with an air vent line 12, containing automatic valve 13, operated by levers 15 connected to a liquid level float 14 in the chamber of the separator 11. This automatically controlled valve 13 permits uniform and constant separation of the air bubbles from the foam produced in the agitator 5 and minimizes the loss of hydrocarbon vapors. It has been found desirable to separate the air from the suspension produced in the agitator 5 prior to the separation of the acid in that after the air is removed the acid may be separated by mere settling.

The air-free mixture of acid and hydrocarbon liquid is withdrawn from the bottom of separator 11, through line 16, into the acid separator 17, which preferably comprises a settler and coalescer, not shown. In the settler the acid and hydrocarbon mixture is allowed to form two liquid phases, namely an upper hydrocarbon phase and a lower acid-sludge phase, the latter being withdrawn through valved line 18. The upper phase is then passed through the above-mentioned coalescer such as a chamber filled with pebbles or the like to remove amounts of acid which did not settle into the acid-sludge phase. After this the hydrocarbon phase usually still contains a trace of acid which must be removed by neutralization. For this purpose it is passed through line 19, into mixer 20, wherein it is mixed with an aqueous alkaline solution such as aqueous sodium hydroxide, sodium carbonate, etc., introduced through valved line 21 in an amount sufficient to neutralize residual acid. The resulting mixture is then passed through line 22 into settler 23.

The neutralized oil is passed through line 25 to the still 26, provided with heating means 27, for redistillation of the sweetened hydrocarbon. The redistilled and final pure and sweetened hydrocarbon product is withdrawn from the top of still 26 through line 28, and the remaining small percent of high boiling impurities is withdrawn through the bottom valved line 29 and usually discarded.

This redistillation of the aromatic hydrocarbons is preferably carried out at a temperature not much above the boiling temperature of the aromatic product, in that excess heat tends to decompose the disulfides formed in the process, thereby souring it again. To avoid this it is also desirable that copper be omitted in the bottom of the still 26, in that copper acts as a catalyst causing decomposition of these disulfides. This latter catalytic effect, however, may be overcome by addition of small amounts of ammonia and air during the distillation. An ordinary steel still has been found satisfactory in the redistillation of sweetened aromatic extracts. The amount of loss of aromatic hydrocarbon by redistillation generally ranges between about 1% and 2½% of the amount redistilled.

The sour aromatic hydrocarbons comprising the feed to this process must be free from the solvent used in extracting them from their respective hydrocarbon distillates. For example, in the extractive distillation of a toluene concentrate in accordance with Dunn et al. U. S. 2,288,126, in the presence of phenolic solvent, the resulting toluene should preferably be caustic alkali treated to remove all traces of the phenol prior to the sweetening treatment of this invention.

Generally, the amount of mercaptan sulfur present in such aromatics obtained by extraction

as described is not more than about .5% by weight and usually is about .3% by weight or less depending upon the type of crude from which it was derived and its prior treatment, although in some cases it may exceed 1%.

The acid employed in treating the aromatic hydrocarbon is preferably relatively concentrated sulfuric acid having a concentration between about 87% and 100%, preferably about 93% to 98%. This acid may be fresh or reconcentrated and refortified spent acid which has primarily been employed in the same or other treating processes. The quantity of acid required is dependent primarily upon the composition of the sour aromatic feed and the content of mercaptans and olefins, as well as on the concentration of the acid employed. Treating temperatures are another factor, optimum temperatures being between 110° F. and 120° F. Thus for example in treating toluene, the acid requirement at 110° F. is only about half that at 85° F. The quantity of acid required may also depend to a minor extent upon the mechanical design of the acid injection apparatus or mixer 2. The quantity of acid usually ranges from about 2 to 50 pounds per barrel of sour aromatic hydrocarbon, depending upon the concentration of the acid, less acid being required the higher its concentration. Roughly, in the range of 87% to 100% concentration, 1% difference in the concentration corresponds to about 2 to 3 pounds per barrel difference in the amount required. Thus, when using 98% to 100% sulfuric acid, amounts required normally vary from about 2 to 15 pounds per barrel; when using 93% to 98% acid the amounts vary between about 5 and 25 pounds per barrel; and when using 87% to 89% acid the requirement is usually on the order of 30 to 50 pounds per barrel. More acid may be employed if color tests, such as the acid heat test, of the resulting sweetened product do not meet specifications.

The following specific example clearly illustrates the process of this invention:

Example I

A toluene concentrate derived by distillation of a West Texas petroleum naphtha was extractively distilled with phenol to produce a sour 1° toluene containing .3% by weight of mercaptan sulfur. Theoretically, one barrel of this sour toluene would require 13.5 cubic feet of air to oxidize all of the mercaptan present in the toluene. This sour toluene was admixed with 20 pounds of 98% sulfuric acid and 2 to 3 cubic feet of air per barrel of toluene in a mixer, agitator and air separator exactly as shown in the drawing. The residence time of the mixture of toluene, acid and air in the agitator was about 35 minutes, and the treating temperature was about 85° F.

After removal of the air in the air separator, the acid was removed by settling and coalescing. The resulting toluene was then neutralized with 2.25 to 2.75 pounds per barrel of 30° Bé. aqueous sodium hydroxide solution and redistilled in a still having a reboiler temperature of not over 300° F., whereby a doctor sweet toluene was produced meeting nitration grade specifications.

The loss of toluene caused by the sweetening treatment amounted to between 1% and 1.5%.

I claim as my invention:

1. In a process for sweetening sour aromatic hydrocarbons of 6 to 10 carbon atoms per molecule containing mercaptans, the steps comprising contacting them at a temperature between 75° and 160° F. with between about 2 and 50 pounds per barrel of sulfuric acid of 87–100% concentration and a controlled amount of air, mechanically agitating said mixture to produce a suspension of said acid and air in said hydrocarbons, maintaining said suspension for a period of about ⅓ to 10 hours and then separating said air and said acid from said suspension, said amount of air being substantially less than the stoichiometrical quantity necessary to oxidize all the mercaptans contained in said hydrocarbons to disulfides.

2. The process of claim 1 wherein said aromatic hydrocarbon is toluene.

3. The process of claim 1 wherein said amount of air is between ⅛ and ½ of said stoichiometrical quantity.

4. The process of claim 1 wherein said sulfuric acid is between about 93 and 98% concentrated.

5. In a continuous process for sweetening sour aromatic hydrocarbons of 6 to 10 carbon atoms per molecule containing mercaptans, the steps comprising contacting them at a temperature between 75° and 160° F. with between about 2 and 50 pounds per barrel of sulfuric acid of 87–100% concentration and a controlled amount of air, mechanically agitating said mixture to produce a suspension of said acid and air in said hydrocarbons, maintaining said suspension for a period of about ⅓ to 3 hours and then separating said air and said acid from said suspension, said amount of air being substantially less than the stoichiometrical quantity necessary to oxidize all the mercaptans contained in said hydrocarbons to disulfides.

6. In a batch process for sweetening sour aromatic hydrocarbons of 6 to 10 carbon atoms per molecule containing mercaptans, the steps comprising contacting them at a temperature between 75° F. and 160° F. with between about 2 and 50 pounds per barrel of sulfuric acid of 87% to 100% concentration and a controlled amount of air, mechanically agitating said mixture to produce a suspension of said acid and air in said hydrocarbons, maintaining said suspension for a period of about 3 to 10 hours and then separating said air and said acid from said suspension, said amount of air being substantially less than the stoichiometrical quantity necessary to oxidize all the mercaptans contained in said hydrocarbons to disulfides.

7. In a process for sweetening sour aromatic hydrocarbons of 6 to 10 carbon atoms and containing mercaptans, the steps comprising contacting them at a temperature between 75° F. and 160° F. with between about 2 and 50 pounds per barrel of relatively concentrated sulfuric acid and a controlled amount of air, mechanically agitating the mixture to produce a suspension of said acid and air in said hydrocarbons, maintaining said suspension for a period of about ⅓ to 10 hours, separating the air from said suspension, and then separating the resulting spent acid from said hydrocarbons, said controlled amount of air being substantially less than the stoichiometric quantity necessary to oxidize all the mercaptans contained in the said hydrocarbons to disulfides.

8. In a process for sweetening sour aromatic hydrocarbons of 6 to 10 carbon atoms and containing mercaptans, the steps comprising contacting them at a temperature between 75° and 160° F. with between about 2 and 50 pounds per barrel of relatively concentrated sulfuric acid and a controlled amount of air, mechanically agitat-

ing the mixture to produce a suspension of acid and air in said hydrocarbons, maintaining said suspension for a period of about ⅓ to 10 hours, separating the air from said suspension, and then separating the resulting spent acid from said hydrocarbons, and distilling said hydrocarbons to produce a pure sweetened product, said controlled amount of air being between ⅛ and ½ the stoichiometric quantity necessary to oxidize all the mercaptans contained in said hydrocarbons to disulfides.

9. The process of claim 6 wherein said aromatic hydrocarbons boil below about 400° F.

10. In a process for sweetening sour toluene containing mercaptans the steps comprising contacting said toluene at a temperature between 75° and 160° F. with between about 2 and 50 pounds per barrel of concentrated sulfuric acid, a controlled amount of air, and a sufficient amount of steam to maintain the temperature of the mixture above about 85° F., mechanically agitating said mixture to produce a suspension of said acid, air, steam and hydrocarbon, maintaining said suspension for a period of ⅓ to 10 hours, separating the air from the suspension, and then separating the resulting spent acid and resulting condensed steam from the hydrocarbons by settling, said controlled amount of air being between ⅛ and ½ the stoichiometric quantity necessary to oxidize all the mercaptans contained in said hydrocarbons to disulfides.

11. The process of claim 8 wherein said temperature is between about 110 and 120° F.

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