PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Process for Regenerating used Alkaline Reagents

We, UNIVERSAL OIL PRODUCTS COMPANY [INC. 1958], a corporation organised under the laws of the state of Delaware, United States of America, of No. 30, Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the regeneration of solutions of sodium or potassium hydroxide which have been used in the treatment of liquid or gaseous hydrocarbon or other organic compositions for the removal of acidic components and particularly sulfur-containing impurities.

Hydrocarbon fractions and other organic compositions which contain sulfur compounds or other acidic impurities are frequently treated with solutions of sodium or potassium hydroxide in order to remove the impurities. These reagents generally are utilized as aqueous solutions containing from about 5% to about 50% by weight of sodium or potassium hydroxide and, when desired, solutizers or solubilizing agents are employed including, for example, alcohols such as methanol and ethanol, phenols, cresols or butyric acid, in order to increase the efficiency of reaction between the acidic components and the alkaline reagent.

The alkaline solutions are especially suitable for the purification of hydrocarbon fractions and particularly sour gasolines including cracked gasoline, straight run gasoline or mixtures thereof, naphtha, jet fuel, kerosene, aromatic solvent, stove oil, range oil, burner oil and distillate fuel oil. Other hydrocarbon fractions which may be similarly treated include lubricating oil and gas oil, as well as normally gaseous hydrocarbon fractions. In addition, other organic materials containing acidic impurities may be treated in this manner, such as alcohols, ketones and aldehydes.

After the hydrocarbon or other organic material has been contacted with the alkaline solution and the acidic components reacted with and/or absorbed in the sodium or potassium hydroxide, the treated fraction is separated from the alkaline solution. The alkaline solution then is regenerated in order to remove the acidic components and to restore the activity of the alkaline reagent for further use in the process.

Regeneration of the used alkaline solution may be effected by steaming at high temperature or by an oxidation treatment which involves contacting the spent solution with air or other free-oxygen-containing gas. However, the use of high temperature is objectionable because it causes extensive damage to the plant equipment. On the other hand regeneration with air has not been satisfactory because efficient regeneration is not obtained. Somewhat better regeneration with air has been effected by subjecting the spent alkaline solution to an oxidising treatment in the presence of various catalysts, but these methods have also been unsatisfactory because of more or less rapid decomposition of the catalysts.

The present invention is based upon the discovery that phthalocyanine catalysts are of superior stability when used to promote the oxidation treatment of the spent alkaline solution. Accordingly the invention provides a process for regenerating a solution of sodium or potassium hydroxide which has been used for the treatment of liquid or gaseous organic compounds to remove acidic components therefrom which comprises subjecting said solution to an oxidising treatment by contacting with air or other free oxygen-containing gas in the presence of a catalyst compris-

[*Price 3s. 6d.*]

ing a metal or metal-free phthalocyanine or a derivative thereof and thereafter separating the oxidation products of said acid components from the solution. It has been found that both the metal-free phthalocyanines and the metal phthalocyanines are effective catalysts in the present process, although the latter are generally preferred.

Cobalt phthalocyanine is a particularly preferred metal phthalocyanine. Other metal phthalocyanines include those of the metals manganese, vanadium, iron, copper, magnesium, zinc, titanium, hafnium, thorium, tin, lead, columbium, tantalum, antimony, bismuth, chromium, molydenum, nickel, palladium, platinum, silver and mercury. These specific phthalocyanines may differ somewhat in their effectiveness. Any suitable metal phthalocyanine may be employed individually, or when desired, a mixture of metal phthalocyanine compounds may be utilized.

In general, the phthalocyanine compounds are not as such readily soluble in aqueous alkaline solutions and, therefore, it is preferable to utilize a derivative thereof. A particularly suitable method for increasing solubility of such phthalocyanines is to prepare sulfonated derivatives. The sulfonated derivatives may be prepared in any suitable manner. For example, the sulfonate of iron phthalocyanine was prepared by reacting iron phthalocyanine with 20% fuming sulfuric acid. In some cases metal phthalocyanine sulphonates are available for purchase in the open market. For example, copper phthalocyanine sulfonate is available commercially.

While the sulfonic acid derivatives are preferred, it is understood that other suitable derivatives may be employed in accordance with the present invention. For example, the carboxylated derivatives may be utilized. One method of preparing these derivatives is by the action of trichloroacetic acid or by the action of phosgene and aluminium chloride on the metal phthalocyanine. In the latter reaction, the acid chloride is formed and is converted to the desired carboxylated derivative by conventional hydrolysis.

While the phthalocyanine compound may be utilized as such, it advantageously may be, and in many cases preferably is, utilized in association with a solid carrier. In some cases, the carrier also may exert a catalytic effect and, in such cases, the combined effect is usually greater than that obtained by the phthalocyanine compound alone. In still other cases, the carrier may serve merely as a means of dispersing the active component and to extend the available surface thereof. As will be shown by the examples below, charcoal is particularly suitable for use as a carrier. Suitable charcoals include bone char, wood charcoal and charcoals made from coconut or other nut shells or fruit pips.

The phthalocyanine compound may be composited with the carrier in conventional manner. For example, in one method, the phthalocyanine compound may be dissolved in a suitable solvent and the solid carrier soaked, suspended or otherwise immersed therein. In another method, the solution of phthalocyanine compound may be sprayed onto the solid carrier. A preferred solvent for this purpose comprises an alcohol and particularly methanol. Other suitable solvents include ethanol, propanol butanol, acetone, methyl ethyl ketone, dimethyl ether and diethyl ether.

Regeneration of the used alkaline solution may be effected either in batch or continuous operation. In a continuous process, for example, the used alkaline solution and air, or other free oxygen-containing gas are continuously supplied to a regeneration zone which contains the phthalocyanine catalyst or to which the phthalocyanine catalyst is introduced. The amount of catalyst to be used in the regeneration zone may vary considerably, depending upon the particular alkaline reagent and the acidic impurities, and may range from 0.0001% to 20% or more by weight of the alkaline reagent. The regeneration may be effected at ambient temperature or at an elevated temperature which generally will not exceed about 95°C. In the regeneration the alkaline solution is substantially restored to its original composition. Thus, for example, in the regeneration of the alkaline solution, any mercaptides present are oxidised to disulfides which are then separated from the alkaline solution. This separation may be accomplished by skimming or by extraction by contacting the reagent with a suitable solvent such as solvent naphtha. The regenerated alkaline solution is withdrawn from the regeneration zone and preferably is continuously or intermittently returned to the treating zone for further use in the purification of the hydrocarbon distillate. The presence of carrier fragments in the hydrocarbon distillate may be objectionable. Therefore, when the phthalocyanine is associated with a carrier, the regenerated alkaline solution preferably is filtered or settled to insure that it is free from entrained carrier particles. In another regeneration procedure the sour alkaline solution together with air or other free oxygen-containing gas is passed over a fixed bed of carrier, for instance coke, on which the catalyst has been absorbed. When using the catalyst in a soluble form, for example as a phthalocyanine disulfonate, the latter may be dissolved in the alkaline solution in a concentration within the range of 0.0001 to 5 weight percent, and simply retained in solution while the reagent circulates through both hydrocarbon treating and regeneration stages. In this latter procedure the treatment of the hydrocarbons with the alkaline solution containing the dis-

solved catalyst takes place in the absence of free oxygen while the regeneration treatment, of course, takes place in the presence of air or other free oxygen-containing gas.

An important advantage to the process of the present invention is that the metal phthalocyanine compounds are exceedingly stable during the regeneration and do not release the metal in a form in which it could subsequently become transferred into the hydrocarbon distillate by contact with regenerated alkaline solution. These metal components, even when present in extremely low concentration in hydrocarbons, act catalytically to accelerate gum formation, and therefore it is of extreme importance to avoid introducing the metal components into a hydrocarbon distillate such as gasoline. In this respect, the metal phthalocyanines of the present invention are considerably more desirable than the metal chelates which have heretofore been suggested for use in the regeneration of alkaline solutions and which do decompose to release metal components.

The regeneration step may be improved by the addition of a liquid which is immiscible with the alkaline solution but capable of dissolving certain organic disulfides. In particular, petroleum fractions often contain thiophenol which is absorbed by the alkaline solution. The oxidation of thiophenol on the surface of the solid catalyst results in the formation of diphenyldisulfide, a solid which occludes the catalyst and destroys its activity. The addition of a small amount of hydrocarbon to the alkaline solution during the air regeneration will dissolve the diphenyldisulfide and render the catalyst active again. When the regenerated alkaline solution is settled, the oil is decanted.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

EXAMPLE I

These runs were made with n-butyl mercaptan and 5% aqueous potassium hydroxide solution. Liquid n-butyl mercaptan was commingled with 5% aqueous potassium hydroxide solution. The concentration of mercaptan was determined in the original as well as in the treated solutions by titrating with silver nitrate solution. In this example the concentration of mercaptan (calculated as —SH) was about 0.4% by weight of the alkaline solution. The phthalocyanine compound used in this example was copper phthalocyanine disulfonate and was utilized in a concentration of 0.01 mol per liter of potassium hyroxide solution.

The alkaline solution containing mercaptan and phthalocyanine compound, as well as a control sample of the alkaline solution and mercaptan but not containing the phthalocyanine compound, were separately stirred vigorously in open air. The percent of the original mercaptans remaining in each solution was determined in the manner hereinbefore set forth after specified periods of contacting, and are reported in the following table:

TABLE I

% of Original Mercaptan Content of Solution Remaining after Regeneration

Time in Minutes	Control Sample	Sample containing phthalocyanine compounds
0	100	100
10	84	43
20	77	21
30	65	4

It will be noted from the data in the above table that the solution regenerated with the phthalocyanine compound contained only 4% of the mercaptan sulfur originally present after 30 minutes, whereas the sample without the metal phthalocyanine compound still had 65% of the original mercaptain sulfur content. This illustrates the considerable efficiency in oxidizing the mercaptans contained in the alkaline solution.

EXAMPLE II

The runs in this example were made in substantially the same manner as described in Example I except that the alkaline reagent used was a 30% potassium hydroxide solution. The results obtained in these runs are reported in the following table:

TABLE II

% of Original Mercaptan Content of Solution Remaining after Regeneration

Time in Minutes	Control Sample	Sample containing phthalocyanine compounds
0	100	100
10	98	77
20	95	42
30	89	21

Here again it will be noted that the phthalocyanine compound (copper phthalocyanine disulfonate) served to considerably accelerate oxidation of the mercaptan.

EXAMPLE III

The phthalocyanine compound illustrated in this example is iron phthalocyanine associated with a commercial charcoal carrier. The runs were made in substantially the same manner as described in Example I, but the catalyst was tested in four different solutions, each containing a different acidic sulfur compound. These compounds were n-butyl marcaptan, sec-butyl mercaptan, thiophenol and hydrogen sulfide. The test solutions were prepared by adding the sulfur compounds to 200 ml. aqueous solutions of KOH (5 to 12%). The catalyst contained 0.02% iron phthalocyanine on charcoal and was prepared by evaporating an 0.1% iron phthalocyanine in methanol solution together with the appropriate amount of charcoal on a steam bath. The catalyst was added to the alkaline solution in a concentration of 0.1% by weight, which is equal to 0.2 ppm (parts per million) of Fe for the whole solution. The results of these runs are reported in the following table in terms of the percentage of the original mercaptan sulfur content of the solution remaining after the indicated periods of time:

TABLE III

Solution No.	1		2		3		4	
% KOH	5%		5%		4%		12%	
Sulfur Compound (Wt. %)	n-butyl mercaptan (0.3%)		sec-butyl mercaptan (0.3%)		thiophenyl (0.3%)		hydrogen sulfide (0.1%)	
Time in Minutes	Cont.	Cat.	Cont.	Cat.	Cont.	Cat.	Cont.	Cat.
0	100	100	100	100	100	100	100	100
15	100	47	68	7.5	100	66	100	59
30	87	4	45	0	100	55	100	22

The very substantial reductions in the amount of sulfur compound remaining in the regenerated potassium hydroxide solutions containing the iron phthalocyanine catalyst relative to the control solutions is readily apparent.

EXAMPLE IV

This example illustrates the effectiveness of commercial cobalt phthalocyanine disulfonate as catalyst for the regeneration of sodium hydroxide solutions (10%) containing various sulfur compounds. The solutions, each 200

m. in volume and containing the concentrations of sulfur compound and catalyst indicated in the table below, were stirred vigorously in the presence of air at 25°C. as in the previous examples. The catalysed solutions are compared with control solutions in terms of the percentage of the original mercaptan sulfur in the solution remaining after the lapse of the indicated periods of time:

TABLE IV

Sulfur Compound	n-butyl mercaptan (0.3%)		tert.-butyl mercaptan (0.3%)		thiophenyl (0.3%)	hydrogen sulfide (0.1%)
Time in Minutes	1 ppm. Cont.	1 ppm. Cat.	10 ppm. Cont.	10 ppm. Cat.	10 ppm. Catalyst	10 ppm. Catalyst
5	95	80	90	50		83
10	90	69	77	24	0	73
15	86	60	66	14		65
30	71	36	36	0		40
50		10	10			10

EXAMPLE V

This example compares the effectiveness of cobalt phthalocyanine and a known catalyst—cobalt disalicylal ethylene diamine—for the regeneration of a 10% sodium hydroxide solution containing 0.2 wt. % of normal butyl mercaptan. The catalysts were first compared as to stability upon dissolution in the alkaline solution. The cobalt phthalocyanine was found by analysis to contain cobalt. The hydroxide solution in a concentration of 50 parts per million, and without formation of a precipitate. When the cobalt disalicylal ethylene diamine was added to 10% sodium hydroxide containing 0.2 wt. % n-butyl mercaptan, a red precipitate separated which was found by analysis to contain cobalt. The same precipitate was formed when the mercaptan was added to the solution after the dissolution of the catalyst. The superior stability of the metal phthalocyanine is therefore readily apparent.

Each of these compounds was incorporated in a concentration of 50 parts per million in a separate portion of a 10% sodium hydroxide solution containing 0.12 wt. % of n-butyl mercaptan, and each solution was then intimately contacted with air at ambient temperature. The sample containing cobalt phthalocyanine became sweet (free from mercaptan sulfur) after four minutes. The sample containing the cobalt disalicylal ethylene diamine required over 140 minutes to become sweet. The superior catalytic properties of the metal phthalocyanine catalyst is therefore also apparent.

EXAMPLE VI

In this example a cobalt phthalocyanine catalyst and a metal-free phthalocyanine catalyst were tested. The latter catalyst was prepared by dissolving a commercial metal-free phthalocyanine powder in methanol, adding charcoal to the mixture and evaporating to deposit the phthalocyanine on the charcoal. The proportions used were such as to produce a final catalyst containing 2.2 wt. % phthalocyanine. In the same way a separate catalyst was prepared containing 2.5 wt. % cobalt phthalocyanine on charcoal. These catalysts were added to separate 200-ml. portions of 10% sodium hydroxide solution in amounts producing a concentration of 250 ppm. of phthalocyanine (based upon the solution). Each solution was then shaken at ambient temperature with 500 ml. of a jet fuel containing .049 wt. % mercaptan sulfur, samples being taken at intervals for analysis. Results were as follows:

TABLE VI

Catalyst	cobalt phthalocyanine	metal-free phthalocyanine
Time in Minutes	% RSH	% RSH
0	.049	.049
5		.012
6	.015	
12	.008	
15		.004
20	.003	
30	.002	

A control test, carried out in the same way but in the absence of catalyst, exhibited substantially no reduction in mercaptan sulfur content.

WHAT WE CLAIM IS:—

1 Process for regenerating a solution of sodium or potassium hydroxide which has been used for the treatment of liquid or gaseous organic compounds to remove acidic components therefrom, particularly a thus used aqueous solution of sodium or potassium hydroxide, which comprises subjecting said solution to an oxidizing treatment by contacting with air or other free-oxygen containing gas in the presence of a catalyst comprising a metal or metal-free phthalocyanine or a derivative thereof and thereafter separating the oxidation products of said acidic components from the solution.

2. Process as claimed in claim 1, characterized in that said solution has been used for the removal of sulfur-containing compounds from hydrocarbon distillates and is regenerated in the presence of a metal phthalocyanine catalyst.

3. Process as claimed in claim 1 or 2, characterized in that the solution of sodium or potassium hydroxide is an aqueous solution.

4. Process as claimed in any of the claims 1 to 3, characterized in that the catalyst comprises a metal phthalocyanine sulfonate.

5. Process as claimed in any of the claims 1 to 3, characterized in that the catalyst comprises a metal phthalocyanine carboxylate.

6. Process as claimed in any of the claims 1 to 3 characterized in that the catalyst comprises a metal or metal-free phthalocyanine or a derivative thereof deposited upon a solid carrier material.

7. Process as claimed in claim 6, characterized in that the solid carrier material is charcoal.

8. Process as claimed in any of the claims 1 to 7, characterized in that the catalyst comprises at least one metal phthalocyanine selected from the phthalocyanine of cobalt, iron and copper.

9. Process as claimed in claim 4, characterized in that the solution of sodium or potassium hydroxide is regenerated in the presence of a catalyst comprising cobalt phthalocyanine disulfonate.

10. Process for regenerating used solutions of sodium or potassium hydroxide substantially as hereinbefore described.

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