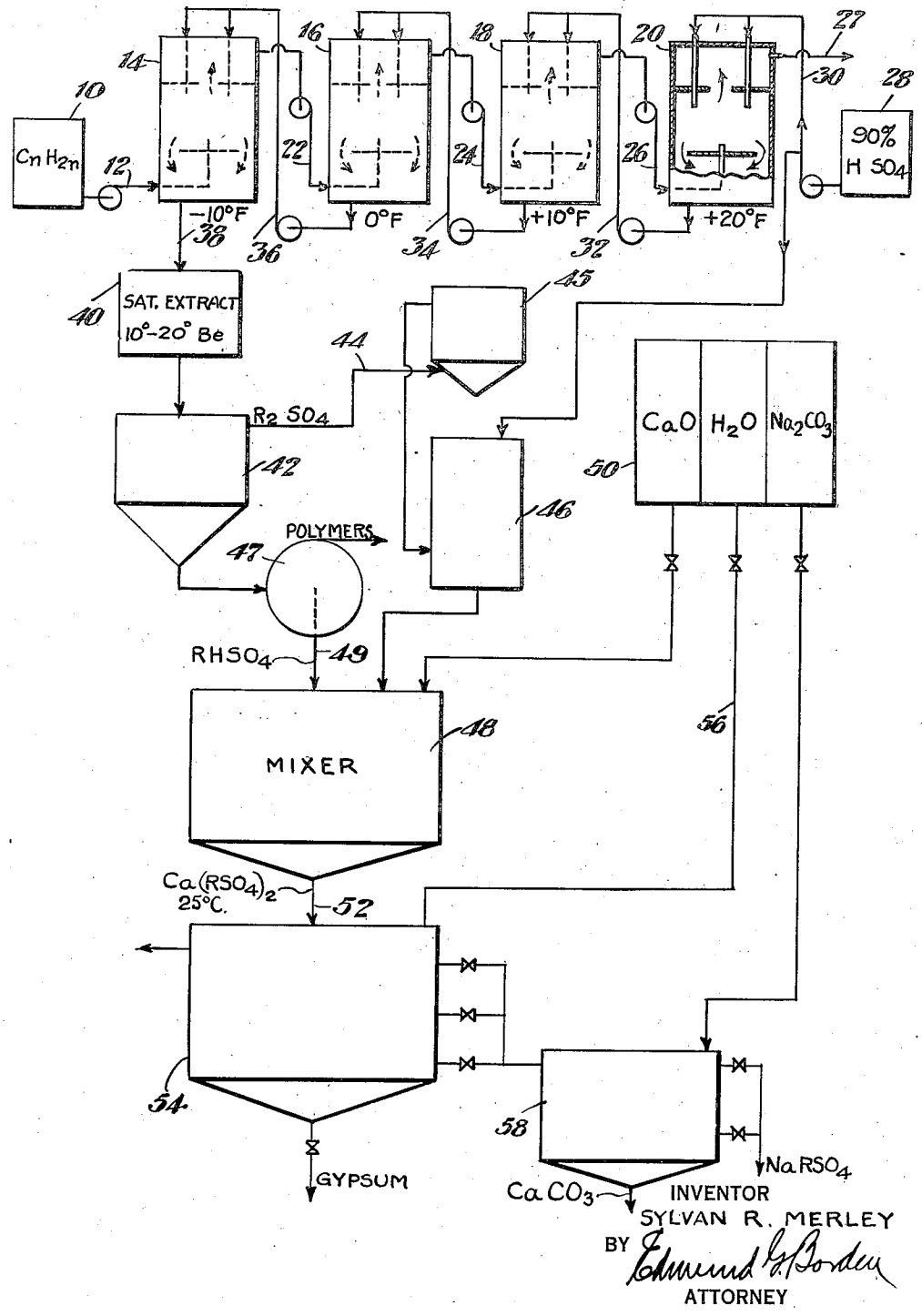
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PROCESS OF PRODUCING METAL ALKYL SULPHATES

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INVENTOR
SYLVAN R. MERLEY
BY Edmund G. Borden
ATTORNEY

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PROCESS OF PRODUCING METAL ALKYL SULPHATES

Sylvan R. Merley, Palmyra, N. J., assignor to Doherty Research Company, New York, N. Y., a corporation of Delaware

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This invention relates to the production of metal alkyl sulphates, and more particularly to the production of metal alkyl sulphates from the olefine content of cracked petroleum products.

In my recently granted U. S. Patent 1,924,616 of August 29, 1933, I have described a process of making organic esters from alkyl sulphates by reacting therewith a substantially anhydrous salt of an organic carboxylic acid in the presence of a stable organic ester, according to which dry alcohols are added to neutralize organic acids formed, and a basic anhydride such as lime is also added to neutralize sulphuric acid. I have found that olefines generally, and particularly hexylene and heavier liquid olefines can be best converted commercially to a specific metal alkyl sulphate by a controlled conversion first to the acid alkyl sulphate, then to the calcium alkyl sulphate, and then to the desired metal alkyl sulphate. I find that it is important, from the standpoint of commercial operation, that the first step of the process be carried out with concentrated sulphuric acid at low temperature so as to produce a high yield of saturated acid alkyl sulphates of 10° to 20° Beaumé gravity and relatively low yields of neutral dialkyl sulphates, olefine polymers and alcohols; and that the second step of the process should also be carried out with anhydrous calcium oxide to avoid loss of acid alkyl sulphate by hydrolysis.

It is a primary object of the present invention to provide a process by which metal alkyl sulphates can be efficiently produced on a commercial scale. A more particular object is to provide a process for producing from high molecular weight olefines (having from six to sixteen carbon atoms in the molecule) a good yield of the corresponding metal alkyl sulphates. A further object is to provide an improved process for producing alkali metal alkyl sulphates from the mono-alkyl esters of sulphuric acid.

With these and other objects in view, the invention consists in the process of making metal alkyl sulphates which is hereinafter described and claimed.

In the accompanying drawing is shown a diagrammatic flow sheet of apparatus in which the various steps of the process may be carried on.

Methods have been heretofore proposed for converting gaseous and liquid olefines into their sulphuric acid esters. In general such methods have the disadvantage, so far as their application to the present invention is concerned, of producing a relatively low yield of mono-alkyl sulphates. A feature of the present invention resides in the control steps employed for converting liquid olefines into a relatively high yield of mono-alkyl sulphates.

The gaseous and liquid products of petroleum cracking may serve, either in crude mixtures or after separation of a particular olefine or group of olefines by fractional distillation, as the source of olefines which are to be converted to mono-alkyl sulphates. For purposes of illustration let it be assumed that mono-hexyl sulphate is to be produced from a liquid fraction of cracked petroleum consisting chiefly of a mixture of hexylenes and hexane. Lower and higher boiling olefines and paraffines, including amylenes and heptylenes, may be present in small quantities.

The hexylene fraction above referred to is pumped from a storage tank 10 through a pipe 12 into the base of the first absorption unit 14 of a series of connected sulphuric acid absorption units 14, 16, 18 and 20. These absorbers 14 to 20 may be of any standard type provided with suitable cooling coils for holding the absorber at a desired low temperature. The absorbers are preferably of the mechanical agitator type arranged for bringing the olefines into intimate contact with a countercurrent flow of an absorbing sulphuric acid solution in a central mixing zone, and having transverse baffle-plates arranged to permit the heavier saturated acid to settle to the bottom of the absorber and the lighter liquid hydrocarbons, stripped of part of the olefine content, to rise to the top of the absorber from which they can pass to the next absorber in the series. That portion of the hexylene-hexane fraction which is not absorbed in the first unit 14 passes by a pipe 22 to the second absorber 16. The unabsorbed hexylene-hexane fraction passes in a similar manner to the absorbers 18 and 20 by means of pipes 24 and 26. The hexane is removed from absorber 20 through a pipe 27. The sulphuric acid which is used to absorb the olefines is pumped from a cooler 28 where it is cooled to just above its freezing temperature, in a reverse direction to the direction of flow of the hexylenes through absorbers 20, 18, 16 and 14 by means of the respective pipes 30, 32, 34 and 36. As the acid advances through the absorbers it becomes more and more saturated so that by the time it leaves the base of absorber 14 through pipe 38 it is comprised chiefly of mono- and dialkyl sulphates.

I have discovered that in order to reduce polymerization of the olefines to a minimum, and to produce as large a yield as possible of mono-alkyl sulphates with a minimum production of

dialkyl and alcohol, each of the absorbers 14 to 20 should be maintained at a low temperature ranging from say −10° F. for absorber 14 to +20° F. for absorber 20; and that a molecular excess of sulphuric acid of 90 to 93 per cent strength should be used in absorption, while passing the olefine and sulphuric acid countercurrently through the absorber units at a rate controlled to produce a saturated acid (after separation of the light liquid hydrocarbons and polymers) of 10 to 20° Beaumé gravity for withdrawal from unit 14 through pipe 38. When using acid of the higher concentration, i. e., 93 per cent acid, the absorbers 14 to 20 may be all advantageously operated at about −10° F. I prefer to operate the absorbers so as to maintain a concentration of about 50 per cent free sulphuric acid in absorber 20, with progressively lower acid concentration in absorbers 18 and 16, and about 5 to 10 per cent free acid in absorber 14. The hexylene or other olefine content of the hydrocarbon mixture treated in the absorbers of course decreases progressively, so that there is substantially no hexylene associated with the hexane which is removed from absorber 20 through pipe 27. The low temperatures at which the absorbers are operated for recovering sulphates of olefines of high molecular weight such as hexylene, heptylene, octylene, or higher members of the series, permit selective absorption of these olefines, while any lower olefines such as propylenes or butylenes pass through the apparatus with the hexane and other paraffins without being appreciably absorbed. In the absorber 14 wherein the hexylene or other olefine first contacts the acid, the percentage of free sulphuric acid is low, and the absorbing liquid consists chiefly of the sulphuric acid esters produced successfully in absorbers 20, 18 and 16. The concentration of hexylene which remains unabsorbed in the hydrocarbon entering the last absorber 20 is so low relative to the volume of unreactive hydrocarbons present, that no serious amount of polymerization occurs despite the fact that concentrated acid is used as the absorption medium therein. The large amount of unreactive hydrocarbon present in absorber 20 apparently serves as a buffer largely preventing polymerization of the higher olefines during their absorption by the acid.

The saturated acid which is removed from absorber 14 through pipe 38 comprises a mixture of mono-alkyl sulphates and dialkyl sulphates, together with some sulphuric acid and a small amount of alcohol produced by hydrolysis of the mono-alkyl sulphates. A considerable percentage of this mixture consists of dialkyl sulphates, or normal sulphates. The saturated acid may be passed from absorber 14 into a storage tank 40; and if separation of the dialkyl sulphates is desired at this point, this may be effected by passing the acid into a separator 42 wherein the dialkyl sulphates are extracted by means of a suitable solvent therefor (such as petroleum hydrocarbon of the type of gas oil) and the extract decanted through draw-off pipe 44. The dialkyl sulphates can be converted to mono-alkyl sulphates by hydrolyzing (in 45) to form the corresponding alcohol, followed by treatment of the alcohol with strong sulphuric acid in 46 at low temperature. The mono-alkyl sulphate thus produced may be combined with that remaining in tank 42 for conversion to metal alkyl sulphates. Whether or not the dialkyl sulphates are separated from the saturated acid by extraction in tank 42, the mixture may be next passed into a centrifuge 47 wherein separation of any occluded light hydrocarbons and polymers is effected.

The remaining components of the mixture are next passed by a pipe 49 into a strong mixing apparatus 48, such as a wheel mill provided with mixing wheels of the type used in mixing viscous material such as paints, equipped with proper cooling means, and the sulfuric acid solution of the acid hexyl sulphate is neutralized by adding thereto a basic anhydride such as calcium or barium oxide, or unslaked lime, from a source 50. The addition of the lime is carefully controlled to prevent the temperature in the mixer from rising above 25° C. Operating temperatures for the mixer as low as 0° C. to 15° C. are even better. The first part of the lime added reacts with uncombined sulphuric acid to precipitate calcium sulphate, and accordingly the mixer 48 must be operated in such a way as to insure thorough disintegration of the calcium sulphate precipitate and thorough contact of the lime with the saturated acid alkyl sulphate to effect complete neutralization thereof without the use of an excess of lime. Since any dialkyl sulphates present are already neutral and fairly stable, their presence may be ignored during the treatment with lime, and for this reason their removal by solvent extraction in separator 42 is not an essential step of the process, though it is an important step from the standpoint of operation to produce maximum yields of the metal alkyl sulphates.

After all of the acid hexyl sulphate has been neutralized with production of the corresponding calcium hexyl sulphate, the charge may be withdrawn from mixer 48 through a pipe 52 into a separator 54 equipped with proper heating and agitating means, and water is added to the calcium hexyl sulphate from a pipe 56. The water combines with the calcium sulphate to produce an insoluble gypsum precipitate, and the calcium hexyl sulphates dissolve in the water—which may be preferably heated to approximately boiling temperature to permit quick settling of the gypsum. Any dialkyl sulphate present is hydrolyzed by the water to produce the corresponding alcohols, which are sparingly soluble in water and can be readily separated from the aqueous calcium hexyl sulphate solution by decantation or by steam distillation. Hydrolysis of the dialkyl sulphates liberates free sulphuric acid, which should be neutralized by lime added in amount sufficient to maintain the mixture slightly alkaline. By digestion of the residual mixture in separator 54, the gypsum settles rapidly to the bottom, permitting removal of the clear calcium hexyl sulphate solution by decantation to storage. Any residue in the separator 54 can be digested with additional hot water and the calcium alkyl sulphate solution decanted. Any gypsum carried in suspension or solution in the decanted solution can be separated therefrom by filtration and by partial vaporization. If recovery of solid calcium hexyl sulphate is desired, the solution is conducted to an evaporator and the water evaporated with production of a crystallized white salt of high purity.

To produce sodium or potassium or other metal hexyl sulphate, the hot solution of calcium hexyl sulphate may be treated in a separator 58 with the corresponding soluble metal carbonate, that is for example with sodium or potassium carbonate. The reaction precipitates relatively insoluble calcium carbonate and forms the corresponding

soluble metal alkyl sulphate. By decantation or filtration and partial evaporation, the calcium carbonate is separated from the sodium or potassium alkyl sulphate, after which the solution of the alkyl sulphate may be evaporated to a supernatent liquid which, on cooling, yields white crystals of relatively pure sodium or potassium alkyl sulphate.

The chemistry involved in the production of sodium hexyl sulphate by the present process is shown by the following equations:

(a) $3C_6H_{12}+2H_2SO_4=C_6H_{13}HSO_4+(C_6H_{13})_2SO_4$

(b) $(C_6H_{13})_2SO_4+2H_2O=2C_6H_{13}OH+H_2SO_4$

(c) $2C_6H_{13}OH+2H_2SO_4=2C_6H_{13}HSO_4+2H_2O$

(d) $2C_6H_{13}HSO_4 + CaCO_3 = (C_6H_{13}SO_4)_2Ca + H_2O+CO_2$

(e) $(C_6H_{13}SO_4)_2Ca+Na_2CO_3=2C_6H_{13}NaSO_4 CaCO_3$

The hydrocarbon oil which is used for separating the dialkyl sulphates from the sulphuric acid solution of the mono-alkyl sulphates has been herein referred to as a solvent for the dialkyl sulphates. The main function of this oil is to extract the dialkyl sulphates from the acid solution. It is possible that the oil does not act as a solvent in a strict sense, but that the action may more closely resemble a physical scrubbing action in which the oil has a greater contact affinity for the dialkyl sulphates than has the acid solution of the acid alkyl sulphates.

A very important feature of the present invention resides in carrying out the neutralization of the acid alkyl sulphate under substantially anhydrous conditions in order to obtain a paying yield of metal alkyl sulphates. During the formation of the acid alkyl sulphates, as well as during the reaction to produce the basic metal alkyl sulphates, the concentration of sulphuric acid present should be such as to have a greater affinity for any water in dilution in the original acid or acid liquor, or for any moisture present in the lime or dry calcium oxide, than the alkyl radical would have in order to be converted (hydrolyzed) to the alcohol; and yet the sulphuric acid must not be present in such concentration, or at such temperature, or both, as to convert the acid alkyl sulphates into polymer bodies or other decomposition products.

The invention having been thus described, what is claimed as new is:

1. The process of making metal alkyl sulphates from dialkyl sulphates which comprises hydrolyzing the dialkyl sulphates to the corresponding alcohol, converting the alcohol to acid alkyl sulphate by reaction with concentrated sulphuric acid in the cold, thereafter reacting the acid alkyl sulphates with a basic anhydride under substantially anhydrous conditions in the cold, and separating the metal alkyl sulphates formed from the residual products of the reaction by extraction with water.

2. The process of making metal alkyl sulphates which comprises mixing a sulphuric acid solution of monoalkyl sulphates and a basic anhydride with vigorous agitation in the cold, controlling the period of agitation and the proportion of reactants to effect neutralization of the free sulphuric acid and complete reaction between the alkyl sulphates and the anhydride, adding water to the mixture in amount sufficient to dissolve the resulting metal alkyl sulphates, heating and agitating the mixture and separating the clear aqueous solution of the metal alkyl sulphate from insoluble products of the treatment.

3. The process of making alkali metal alkyl sulphates which comprises mixing a sulfuric acid solution of mono-alkyl sulphate and anhydrous calcium oxide with vigorous agitation in the cold, adding water to the mixture and heating, separating the resulting aqueous solution of calcium alkyl sulphate from insoluble products of the treatment, and adding an alkali metal carbonate to the calcium alkyl sulphate solution in amount sufficient to precipitate the calcium as calcium carbonate and convert all the calcium alkyl sulphate to alkali metal alkyl sulphate.

4. The process of making metal alkyl sulphates which comprises absorbing olefins in an excess of concentrated sulphuric acid at a temperature as low as freezing point of the acid will permit, controlling the concentrations of olefins and acid and the period of contact to yield a saturated alkyl sulphate of 10° to 20° Beaumé gravity, mixing a basic anhydride with the resulting acid alkyl sulphate solution with vigorous agitation in the cold, adding water to the mixture and heating, and separating the resulting aqueous solution of metal alkyl sulphate from insoluble products of the treatment.

5. The process of making metal alkyl sulphates which comprises absorbing olefin hydrocarbons in an excess of 90 to 93 per cent sulphuric acid at a temperature as low as the freezing point of the acid will permit, controlling the concentrations of olefins and acid and the period of contact to produce a saturated alkyl sulphate solution of 10° to 20° Beaumé gravity, mixing anhydrous calcium oxide with the acid alkyl sulphate solution with vigorous agitation in the cold, adding water to the mixture and heating, separating the aqueous solution of calcium alkyl sulphate from insoluble products of the treatment, and adding a soluble metal carbonate to the solution in amount sufficient to convert the calcium alkyl sulphate into the desired metal alkyl sulphate and an insoluble precipitate of calcium carbonate.

6. The process of making metal alkyl sulphates which comprises absorbing olefines in an excess of concentrated sulphuric acid at a temperature of about −10° F. thereby producing a mixture of dialkyl sulphates and mono-alkyl sulphates, extracting the mixture with a selective liquid hydrocarbon solvent for the dialkyl sulphates and separating the hydrocarbon extract from the residual sulfuric acid solution of acid alkyl sulphates, mixing a basic anhydride with the acid alkyl sulphate with vigorous agitation in the cold, adding water to the mixture in amount sufficient to dissolve the resulting metal alkyl sulphate, and separating the solution of metal alkyl sulphate from insoluble products of the treatment.

SYLVAN R. MERLEY.