

UNITED STATES PATENT OFFICE.

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SULFONIC-ACID SALT AND PROCESS OF MAKING SAME.

SPECIFICATION forming part of Letters Patent No. 671,135, dated April 2, 1901.

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To all whom it may concern:

Be it known that I, LUDWIG OTTO HELMERS, a subject of the German Emperor, residing at Hamburg, in the German Empire, have invented certain new and useful Improvements in Sulfonic-Acid Salts of Alkaline Earthy Metals and Metals Proper and Their Sulfonic Acids and Processes of Making Same, of which the following is a specification.

By the specifications of the United States Patents Nos. 318,663 and 495,343 it has been disclosed that the sulfonized product obtained by the action of sulfuric acid on sulfureted hydrocarbons and neutralized by means of an alkali is soluble in water. In the specification of my United States Patent No. 525,784 I have furthermore set forth that this sulfonized product neutralized by means of alkalis consists of two constituents—namely, of the sulfonic-acid alkaline salts *per se*, soluble in water, and of sulfone-like bodies *per se*, insoluble in water—and that these latter bodies may be maintained in aqueous solution only by the former—the sulfonic-acid alkaline salts.

If the sulfonized product obtained by the reaction of sulfuric acid upon sulfureted hydrocarbons is neutralized with the oxid, hydroxid, or carbonate of an alkaline earth or heavy metal, or if the salt of an alkaline earthy metal or metal proper is added to the solution of the sulfonized product which is neutralized by means of an alkali, it yields a precipitate which contains not only the above-mentioned sulfone-like bodies *per se*, insoluble in water, but also the total amount of the sulfonic acids, as alkaline-earth or metals salt, respectively, since the sulfonic acids obtained by the reaction of sulfuric acid upon sulfureted hydrocarbons are formed with alkaline-earth and heavy-metal combinations which are insoluble in water, as explained in the specifications of my United States Patents Nos. 624,027 and 624,028 and also in German Patent No. 72,049.

From a careful investigation recently performed it has been proven that a considerable part of the sulfonic acids is not precipitated by alkaline earth and heavy metals and that therefore the sulfonized product also contains acids the alkaline-earth and heavy-metal

salts of which are soluble in water. These acids and their respective alkaline-earth and heavy-metal salts may be easily obtained if the sulfonized product obtained from the reaction of sulfuric acid upon sulfureted hydrocarbons is neutralized in an aqueous solution with the oxid, hydroxid, or carbonate of an alkaline earth or heavy metal and after a certain time the liquid decanted from the precipitate, then the acid in the solution set free therefrom by precipitating the base, and finally evaporating the filtrate. The so-obtained sulfonic acids, which form soluble alkaline-earth and heavy-metal salts, are distinguished by their high percentage in sulfur, (they contain generally twenty-one per cent. of sulfur as against fifteen per cent. in the insoluble product;) further, on account of their highly-acidic character, (they combine, for example, with nearly eight per cent. of calcium, while the product insoluble in water only contains two and one-half per cent. of calcium,) and, finally, on account of the capability of their salts to convey substances insoluble in water, such as cresol, in far larger quantity into an aqueous solution than the alkali salts, which correspond to the insoluble alkaline-earth and other metallic salts.

The acids, as well as their salts, furthermore possess strong reducing properties of such a capacity that the salts with an easily-reducible base, such as the silver or mercury salts, cannot be produced in a permanent form. In view of the great importance these salts would have in their strong antiseptical and bactericidal effect attempts have been made to convert the acids in such a manner that permanent metallic salts could be obtained therefrom. In the course of further experiments it has now been proven that the acids giving soluble alkaline-earth salts will lose their unsaturated character on treating the same with oxidizing means and that these oxidized acids will, in fact, form permanent salts soluble in water with heavy metals, even with such metals the oxids of which are easily reducible.

The following example may more fully elucidate the production of the permanent silver salt: One kilogram of the sulfonized product obtained by the reaction of sulfuric acid upon

Seefeld mineral oil is dissolved in about two to three liters of water, and this solution at a raised temperature is neutralized with carbonate of barium. After cooling this mixture the brown-colored liquid is decanted from the precipitate and evaporated to a small volume. The barium is precipitated from the solution by means of the calculated quantity of sulfuric acid and the filtrate now containing the sulfonic acid in solution, heated for some time with about 0.4 liter of commercial peroxid of hydrogen, (containing three per cent. H_2O_2 .) The color of the liquid, at first green, soon turns into a reddish brown. The solution of the oxidized acid is then evaporated. The residual acid thus resulting forms a dark brown syrup-like nearly odorless mass, which is easily soluble in water.

In order to produce the silver salt, the aqueous solution of the oxidized acid is neutralized with argentic oxid or carbonate, then filtered from the undissolved constituents, and the filtrate dried by evaporation or otherwise. The residual silver salt appears as a brown mass, which is easily pulverized and readily soluble in water. Further experiments have shown that the same acid and permanent metal salts will also result from direct oxidation of the sulfonized product, which is obtained by treating sulfureted hydrocarbons with sulfuric acid. The aqueous solution of such oxidation product is then to be neutralized by means of the oxid, hydroxid, or carbonate of an alkaline earth or heavy metal and filtered off from the insoluble alkaline-earth or heavy-metal salts. The oxidized acid is now directly obtained by precipitating the base from the solution. The acid thus obtained and the salts resulting from neutralizing the former fully correspond to the products hereinbefore described. If, for instance, chromic acid is applied as oxidizing agent, the process will be as follows: One kilogram of the sulfonized product resulting from the reaction of sulfuric acid upon a sulfureted hydrocarbon is dissolved in about two liters of water, and to this solution is gradually added an aqueous solution of about fifty grams of chromic acid and forty grams of sulfuric acid. After the chromic acid is reduced the liquid standing above the precipitate is decanted off and mixed with milk of lime in order to precipitate chromic oxid and sulfuric acid, whereupon the filtrate is evaporated to a small volume. The sulfate of calcium remaining in the solution is thereupon precipitated by the addition of spirit, then a certain quantity of sulfuric acid corresponding to the content of lime is added, again filtered off from the separated calcium sulfate, and finally the spirit distilled from the filtrate. The aqueous solution now containing the free oxidized acid is neutralized with silver oxid. After the evaporation of the wa-

ter, which is preferably performed *in vacuo*, the silver salt remains as a brown easily-pulverizable residue, fully corresponding with the product obtained according to the first-mentioned example.

Having thus described my invention, what I claim as new therein, and desire to secure by Letters Patent, is—

1. The process of producing sulfonic acids, forming permanent metallic salts soluble in water, which consists in neutralizing the sulfonized compound obtained by the action of sulfuric acid on sulfureted hydrocarbons with a suitable metallic base, filtering off the liquid from the insoluble salts, oxidizing the filtered solution, setting free the sulfonic acid by precipitating the base, and evaporating the filtrate to dryness, substantially as described.

2. The process of producing permanent metallic salts soluble in water, which consists in neutralizing the sulfonized compound obtained by the action of sulfuric acid upon sulfureted hydrocarbons with an alkaline-earth base, filtering off the liquid from the insoluble salts, oxidizing the filtered solution, setting free the sulfonic acid by precipitating the alkaline earth, neutralizing the filtrate with a metallic base and evaporating the liquid to dryness, substantially as described.

3. The process of producing sulfonic acids, forming permanent metallic salts soluble in water, which consists in oxidizing the sulfonized compound obtained by the action of sulfuric acid on sulfureted hydrocarbons, neutralizing the oxidized product with a suitable metallic base, filtering off the liquid from the precipitated insoluble salts, setting free the sulfonic acid by precipitating the base, and evaporating the filtrate to dryness, substantially as described.

4. The process of producing permanent metal salts soluble in water, which consists in oxidizing the sulfonized compound obtained by the action of sulfuric acid on sulfureted hydrocarbons, neutralizing the oxidized product with an alkaline-earth base, filtering off the liquid from the precipitated insoluble salts, setting free the sulfonic acid by precipitating the earth alkali, neutralizing the filtrate with a metallic base and evaporating the liquid to dryness, substantially as described.

5. As a new product of manufacture, the herein-described sulfonic-acid salts, consisting of a metal proper and an oxidized sulfonic-acid compound derived from sulfureted hydrocarbons combined with sulfuric acid, which salts are of a brown color, soluble in water and permanent in their solution.

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Witnesses:

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