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MANUFACTURE OF STYPHNIC ACID SALTS

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This invention relates to the manufacture of styphnic acid and certain of its salts, and contemplates improvements and refinements in the production of styphnic acid, the practice of which results in a product adapted to be made into salts having certain desirable properties and characteristics.

The present application is a continuation in part of my prior co-pending application, Serial No. 207,782, filed May 13, 1938, which is a division of application Serial No. 674,049, filed June 2, 1933, now Patent No. 2,137,234, November 22, 1938.

More specifically, the invention contemplates the control of the shape and form of the crystals of certain salts of styphnic acid, particularly basic lead styphnate, and certain methods in the manufacture of styphnic acid which enable the acid to form salts having novel and desirable crystal shapes.

The manufacture of basic lead styphnate, and particularly a red crystalline form thereof is described in this applicant's Patent No. 1,942,274, January 2, 1934. It may be briefly summarized as follows:

A solution of styphnic acid and sodium hydroxide, in the proportions of 12.2 grams of styphnic acid and 8 grams of sodium hydroxide in 400 c. c. of water, is dropped into a lead nitrate solution of the concentration of about 35 grams of lead nitrate in 350 c. c. of water. The temperature is maintained between 60° and 70° C., and the styphnic acid-sodium hydroxide solution is at first dropped into the lead nitrate solution very slowly. The first precipitate is a previously known yellow amorphous or partly amorphous basic lead styphnate which, if the sodium hydroxide-styphnic acid solution is at first introduced quite slowly, changes over to a heavier red crystalline basic lead styphnate which quickly settles out.

When in the practice of the process above outlined ordinary styphnic lead is used, the crystals of basic lead styphnate are rather thick hexagonal plates. They are less fragile and sensitive to friction and shock than the previously known yellow needle crystals. The present invention comprises the discovery of other crystalline forms of basic lead styphnate, and methods for producing basic lead styphnate in these forms. The novel crystal shapes result from the use of styphnic acid made in accordance with certain procedures constituting a part of the present invention. The manufacture of ordinary styphnic acid will first be briefly described:

The raw material is resorcline ($C_6H_4(OH)_2$). By treatment with concentrated sulphuric acid, resorcline is sulphonated to resorcine-di-sulphonic acid, $C_6H_2(OH)_2(SO_3H)_2$. The resorcine-di-sulphonic acid is then nitrated with concentrated nitric acid. The precipitated styphnic acid is separated from the residue by centrifugal action or by filtration, and subsequently washed, first with a dilute mineral acid and then with water. If the sulphonation of the resorcline is complete, the resulting product is pure styphnic acid of a bright yellow color and low gravimetric density, from which crystalline salts are formed only with great difficulty.

The present invention comprises the discovery that the character of the styphnic acid may be altered in such a way as to control the crystal shape of the salts which it forms by the addition, during the operation of sulphonating, of small amounts of certain foreign substances. Such variations in the styphnic acid and in the crystal shape of its salts, particularly the basic lead salt, are produced by the use of any one of a number of different substances. Moreover, each substance has the property of producing its own characteristic effects and crystal shape, each of these shapes differing from the others. For example, if to a batch comprising 110 grams of resorcline and 460 c. c. of 98% sulphuric acid there be added 10 c. c. of concentrated nitric acid, the resulting styphnic acid is darker in color and less voluminous and its salts have different physical properties. The further addition of .1 gram of tri-oxy-methylene results in a styphnic acid which yields its basic lead salt in crystals of a shape differing very substantially from the usual crystals of this salt. Said crystals are somewhat elongated square or rectangular prisms, as distinguished from the usual hexagonal plates, and appear to be more sensitive to shock and friction than the hexagonal plates. Two opposite faces of the rectangular-prismatic crystals appear to be substantially square, while the other faces are rectangles having a length of the general order of three or four times their width.

The use of catechol in place of tri-oxy-methylene produces a styphnic acid whose basic lead salt likewise forms in square prismatic crystals, but these crystals are much shorter (more nearly cubical) than those resulting from tri-oxy-methylene. The procedure is as follows: The crystal controlling agent is preferably introduced into the sulphonating sulphuric acid. Just as with tri-oxy-methylene, improved results

are secured if a small amount of nitric acid is also used. In 460 c. c. of 98% sulphuric acid there is mixed 10 c. c. of concentrated nitric acid and 5 gram of crystalline catechol. The acid thus prepared is poured over 110 grams of resorcline, this being the usual procedure in the sulphonation of resorcline. The manufacture of styphnic acid and the salts thereof, such as the basic lead styphnate, is then completed in the manner heretofore described.

The use of glucose in place of tri-oxy-methylene or catechol as above described produces greatly elongated rectangular crystals of the salts. For this purpose, crystalline glucose is used in exactly the same manner as tri-oxy-methylene or catechol, .25 gram thereof being a desirable quantity for additional to 460 c. c. of 98% sulphuric acid and 10 c. c. of concentrated nitric acid, the mixture being used in the sulphonation of 110 grams of resorcline.

The use of phenol in place of any of the addition agents above-mentioned likewise produces a characteristic crystal, differing from that produced by any of the other addition agents. These crystals are substantially rectangular in cross section and extremely long. A desirable quantity is 1 gram of crystalline phenol with 10 c. c. of concentrated nitric acid in 460 c. c. of 98% sulphuric acid, the mixture sulphonating 110 grams of resorcline.

The use of aluminum in the same manner produces crystals which are very nearly cubical and exceptionally clean. 1 gram of powder of aluminum and 10 c. c. of concentrated nitric acid are added to 460 c. c. of 98% sulphuric acid, which is then used for the sulphonation of 110 grams of resorcline.

The use of glacial acetic acid as an addition agent produces a striking effect in that the salt crystals are short, rectangular prisms with rounded corners, somewhat resembling the crystals of normal lead styphnate. Such crystals are produced from styphnic acid, in the preparation of which about 5 c. c. of glacial acetic acid and 10 c. c. of concentrated nitric acid have been added to 460 c. c. of 98% sulphuric acid, which is then used for the sulphonation of 110 grams of resorcline.

The use of water as an addition agent produces a salt in crystals which are nearly cubical and exceptionally firm and dense. Such crystals are produced from styphnic acid in the preparation of which about 75 c. c. of water and 10 c. c. of concentrated nitric acid are added to 460 c. c. of 98% sulphuric acid, which is then used for the sulphonation of 110 grams of resorcline.

It should be remembered that the foreign substance is introduced in the sulphonation operation in the preparation of styphnic acid, and that the described crystal shapes are those of the salts, particularly the basic lead salt, of the acid produced by the nitration of resorcline di sulphonic acid made in the presence of the foreign substance.

No satisfactory theoretical explanation of these effects can be offered. The foreign substances which cause them do not fall within any recognized class, or appear to have any property in common other than their ability to change the crystal shape of basic lead styphnate from hexagonal to generally rectangular. Limited oxidation of the resorcline or the resorcline-di-sulphonic acid may be a factor, but oxidation alone cannot account for effects which are individual to the different addition agents.

What is claimed is:

1. In the manufacture of a lead salt of styphnic acid by the sulphonation and nitration of resorcline to styphnic acid and the subsequent formation of a crystalline salt therefrom, the step which comprises the addition of glucose to the sulphonating acid, whereby in a subsequent step said lead salt is formed in crystals of a configuration characteristic to said addition.

2. In the manufacture of basic lead styphnate by a process including the sulphonation and nitration of resorcline to styphnic acid and the subsequent formation of a crystalline salt therefrom, the step which comprises the addition of glucose to the sulphonating acid, whereby in a subsequent step said basic lead styphnate is formed in crystals of a configuration characteristic to said addition.

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