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MANUFACTURE OF STYPHNIC ACID SALTS

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3 Claims. (Cl. 260—435)

This invention relates to the manufacture of styphnic acid 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 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 acid 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 resorcine ($C_6H_4(OH)_2$). By treatment with concentrated sulphuric acid, resorcine 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 resorcine 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 resorcine 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; while, if glucose is similarly used the resulting rectangular crystals are greatly elongated. The use of phenol in making the acid likewise results in a salt in very long crystals of substantially rectangular cross-section. The addition of 75 c. c. of water during the sulphonation produces an acid whose salt form in crystals which are nearly cubical and exceptionally firm

and dense. The addition of a small amount of aluminum produces salt crystals which are nearly cubical and unusually clean. The use of 95% sulphuric acid, instead of 98%, results in a mixture of amorphous salt and comparatively short rectangular crystals. Acetic acid produces a striking effect in that the salt crystals are large short rectangular prisms with rounded corners, somewhat resembling the crystals of normal lead styphnate.

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 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 tetragonal. Among themselves their effects differ in that each produces a crystal which is easily identified and distinguished from the crystals produced by the others. Tri-oxymethylene, catechol, glucose and aluminum, all tend to form oxides; hence should have a reducing action. On the other hand, phenol and acetic acid are not such reducing agents. Diluting the sulphuric acid and adding water tend to limit the amount of water that can be absorbed by the sulphuric acid, hence to lower the concentration of the nitrating nitric acid and increase its oxidizing effect. Thus, the general effect (production of tetragonal crystals) cannot be definitely attributed either to oxidation or reduction, nor is it limited to either organic or inorganic compounds.

What is claimed is:

1. In the manufacture of salts of styphnic acid by the sulphonation of resorcine with sulphuric acid of a concentration of substantially 98%, the nitration of the sulphonated resorcine to styphnic acid, and the subsequent production of a crystalline salt therefrom, the process which comprises the addition of water during the sulphonation, whereby said salt is formed in crystals of a configuration characteristic to said addition.

2. In the manufacture of salts of styphnic acid by the sulphonation of resorcine with sulphuric acid of a concentration of substantially 98%, the nitration of the sulphonated resorcine to styphnic acid, and the subsequent production of a crystalline salt therefrom, the process which comprises the addition of substantially 75 c. c. of water to said 460 c. c. of 98% sulphuric acid, whereby said salt is formed in crystals of a configuration characteristic to said addition.

3. The manufacture of basic lead styphnate by the process including the sulphonation of resorcine by sulphuric acid of a concentration of substantially 98%, the nitration of the sulphonated product to styphnic acid, and the subsequent formation of a crystalline salt therefrom, the process which comprises the addition of water during the sulphonation, whereby said basic lead styphnate is formed in crystals of a configuration characteristic to said addition.

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