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PROCESS FOR THE SULPHONATION OF
ALPHA - AMINOANTHRAQUINONE COM-
POUNDS

James Ogilvie, Buffalo, N. Y., assignor to Allied
Chemical & Dye Corporation, New York, N. Y.,
a corporation of New York

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The present invention relates to a process for the preparation of sulphonates of alpha-aminoanthraquinone compounds and more particularly to a process for the preparation of 1-aminoanthraquinone-2-sulphonic acid in the form of the free acid or its salts; e. g., the sodium salt.

The preparation of 1-aminoanthraquinone-2-sulphonic acid has occupied the attention of many investigators, and a number of methods have been proposed involving both indirect processes and processes in which 1-aminoanthraquinone is sulphonated directly.

Owing to the fact that direct sulphonation of 1-aminoanthraquinone by ordinary sulphonation methods, such as heating with sulphuric acid or oleum, leads to the formation of undesirable by-products, such as oxidation products and isomers, thus reducing the yield and purity of 1-aminoanthraquinone-2-sulphonic acid obtainable, it has been proposed to convert 1-aminoanthraquinone to 1-aminoanthraquinone-2-sulphonic acid by various modified direct sulphonation methods. For example, it has been proposed to sulphonate 1-aminoanthraquinone with a mixture of oleum and an alkali metal or alkaline earth metal sulphate; to convert the acid sulphate of 1-aminoanthraquinone, formed by heating 1-aminoanthraquinone with about an equimolecular amount of sulphuric acid, to 1-aminoanthraquinone-2-sulphonic acid by heating it in the solid phase at a high temperature; and to form 1-aminoanthraquinone-2-sulphonic acid by heating 1-aminoanthraquinone with an acid alkali metal sulphate at a high temperature. The yields obtainable by these processes are not as high as could be desired and the 1-aminoanthraquinone-2-sulphonic acid is often obtained in admixture with undesirable by-products.

It has also been proposed to mix 1-aminoanthraquinone with a substantially equimolecular quantity of chloresulphonic acid at a low temperature adapted to form an intermediate compound and then to heat the intermediate compound at a temperature adapted to convert it to 1-aminoanthraquinone-2-sulphonic acid. Thus, in U. S. P. 2,135,346 of November 1, 1938, the 1-aminoanthraquinone is mixed with the chloresulphonic acid in an inert high-boiling solvent at a low temperature and then heated to complete the reaction; and in U. S. P. 2,251,688 of August 5, 1941, the 1-aminoanthraquinone is ground in a ball-mill with the chloresulphonic acid at a low temperature and the resulting mixture is then heated to complete the reaction.

While processes of this type have the advantages of producing high yields of products which are free from inorganic salts and other impurities present in products of other processes, they have disadvantages from an operating standpoint. For example, the process of U. S. P. 2,135,346 requires the use of a large amount of an expensive solvent whose separation from the product and recovery for reuse complicate the process and require additional equipment, with attendant expense; and the process of U. S. P. 2,251,688 requires special apparatus.

It is an object of the present invention to provide a process for the preparation of 1-aminoanthraquinone-2-sulphonic acid compounds by the direct sulphonation of 1-aminoanthraquinone compounds in which the 2-, 3- and 4-positions are unsubstituted, which process is characterized by simplicity and economy in operation and the high yields obtainable.

A further object of the invention is to provide a process for the preparation of 1-aminoanthraquinone-2-sulphonic acid involving the sulphonation of 1-aminoanthraquinone, which process is characterized by high yields of 1-aminoanthraquinone 2-sulphonic acid, economy of operations, and the avoidance of undesirable by-products.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

It has been found in accordance with the present invention that 1-aminoanthraquinone-2-sulphonic acid compounds can be prepared by heating 1-aminoanthraquinone compounds with chloresulphonic acid in sulphuric acid monohydrate as the reaction medium.

The invention will be further explained in connection with the sulphonation of 1-aminoanthraquinone to produce 1-aminoanthraquinone-2-sulphonic acid. It is pointed out, however, that the invention is not limited to preparation of the latter but includes the sulphonation of other aminoanthraquinone compounds in which the amino group is in the 1-position, the 2-, 3-, and 4-positions are unsubstituted, and the 5-, 6-, 7-, and 8-positions are substituted or unsubstituted.

In carrying out the sulphonation of 1-aminoanthraquinone in accordance with a preferred method of procedure, 1-aminoanthraquinone is dissolved in a limited amount of sulphuric acid monohydrate; the solution is heated to a sulphonation temperature and, while the solution is maintained at about the said sulphonation temperature, chloresulphonic acid is added to the solution in an amount substantially corresponding to an equimolecular quantity based on the

aminoanthraquinone; thereafter the mixture is maintained at about the sulphonation temperature until the conversion of the 1-aminoanthraquinone to 1-aminoanthraquinone-2-sulphonic acid has taken place; and the resulting 1-aminoanthraquinone-2-sulphonic acid is then recovered from the reaction product.

The process of the invention also can be carried out by mixing the chlorsulphonic acid with the 1-aminoanthraquinone and sulphuric acid monohydrate and then heating the mixture to the sulphonation temperature; but in such a variation, inasmuch as 1-aminoanthraquinone is not wholly soluble at ordinary temperatures in the relatively small amounts of sulphuric acid monohydrate preferably used in accordance with the invention, the yields and quality of 1-aminoanthraquinone-2-sulphonic acid obtained are decreased somewhat by side reactions which occur in the course of heating the mixture to the sulphonation temperature, although other practical advantages of the invention are retained.

In effecting the sulphonation according to the present invention, the reaction mixture or solution is usually maintained at a temperature lying between the limits of about 120° and about 160° C. At materially lower temperatures (e. g., at 100° C. or below), the rate of sulphonation is undesirably slow in comparison with the rate at which side reactions occur with consequent diminution in the yield of 1-aminoanthraquinone-2-sulphonic acid. Hydrogen chloride is evolved during the sulphonation reaction. The reaction mass is usually heated until the evolution of hydrogen chloride ceases, when sulphonation is considered at an end. In general, when substantially equimolecular proportions of chlorsulphonic acid and 1-aminoanthraquinone are employed in the process of the present invention, about two-thirds of the initial 1-aminoanthraquinone is sulphonated, and about one-third is recovered unchanged, irrespective of other variables, e. g., time and temperature of the sulphonation reaction. Residual unsulphonated 1-aminoanthraquinone may be used in a repetition of the process.

In order to minimize side reactions, the chlorsulphonic acid is preferably added, substantially at the same rate as it is consumed, to the heated solution of 1-aminoanthraquinone in sulphuric acid maintained at the selected, suitable reacting temperature. This may be done, for example, by adding the chlorsulphonic acid at a uniform rate to the solution of 1-aminoanthraquinone in sulphuric acid during about 4 hours at about 120° C., during about 3 hours at about 130° C., or during about 1 hour at about 150° C. to 160° C., and maintaining the resulting mass at the particular temperature for about an additional quarter of an hour to insure complete utilization of the added chlorsulphonic acid.

In the interest of avoiding large batch volumes, and of economically and efficiently carrying out the sulphonation, the sulphuric acid monohydrate is preferably used in an amount approximately equal to the weight of the 1-aminoanthraquinone. With such an amount of sulphuric acid, when a mixture of 1-aminoanthraquinones is employed comprising essentially 5 parts or more of 1-aminoanthraquinone recovered from a previous sulphonation reaction of the present invention, and 95 parts or less of commercial 1-aminoanthraquinone (containing 97 to 100 per cent of pure 1-aminoanthraquinone, the remainder being insoluble material as de-

termined by extraction with monochlorobenzene in a Soxhlet extractor), the 1-aminoanthraquinone and reaction products are completely dissolved in the reaction mass at temperatures between 120° and 160° C. When, under such conditions, a relatively pure grade of 1-aminoanthraquinone (such as the aforementioned commercial product) is employed alone as initial material, considerable amounts of crystalline material (presumably 1-aminoanthraquinone-2-sulphonic acid) form in the reaction mass as sulphonation proceeds, but the reaction mass still remains fluid and easily agitated. Satisfactory yields and quality of 1-aminoanthraquinone-2-sodium sulphate are also obtainable by employing from about 0.8 part to about 2 parts of sulphuric acid monohydrate per part by weight of 1-aminoanthraquinone. When the quantity of sulphuric acid monohydrate used is substantially increased over 2 parts per part of 1-aminoanthraquinone by weight, the quality of the product becomes progressively poorer. Thus, it has been found that when 4 or more parts of sulphuric acid monohydrate per part of 1-aminoanthraquinone are used, although ortho-sulphonation still occurs, the excess sulphuric acid tends to convert appreciable amounts of the 1-aminoanthraquinone to unidentified by-products (which may be polysulphonates or oxysulphonates of 1-aminoanthraquinone) and by such action reduces the yield of 1-aminoanthraquinone-2-sulphonic acid (on the basis of both the total amount of 1-aminoanthraquinone employed and the amount consumed), and produces a very poor quality of sulphonation product. The use of substantially less than 0.8 part of sulphuric acid monohydrate per part of 1-aminoanthraquinone is not preferred, since under such conditions it becomes increasingly difficult to maintain a homogeneous, fluid reaction mass, with the result that the yield and quality of 1-aminoanthraquinone-2-sulphonic acid become progressively poorer.

Sulphuric acid monohydrate employed as the solvent in the present invention, includes commercial sulphuric acid monohydrate, which is usually of 98 to 100 per cent strength. In general, weaker sulphuric acid should be avoided since the excess water present will react with the chlorsulphonic acid (forming sulphuric acid and hydrogen chloride) thus reducing the amount of chlorsulphonic acid available for sulphonating the 1-aminoanthraquinone. Further, although sulphuric acid having a greater content of sulphur trioxide than 100% sulphuric acid (namely, oleum) could be used, in general it is undesirable since it tends to promote side reactions and reduce the yield of the product.

While the invention is not limited to any theoretical explanation, it seems probable that the sulphuric acid used as a solvent forms a sulphate with the 1-aminoanthraquinone which is stable under the sulphonating conditions. In view of this, the subsequent entry of the sulpho group into the ortho-position to the amino group is surprising since it is known that the conversion of an aromatic amine to an aromatic amine sulphate tends to paralyze the normal ortho-para orienting influence of the amino group and causes the entering group to orient meta (see Conant "The Chemistry of Organic Compounds" (1934) pages 366 and 391). The process of the present invention is also surprising in view of the fact that it is known that the reaction of oleum with 1-aminoanthraquinone dissolved in sulphuric acid

monohydrate at corresponding moderate temperatures produces substantial amounts of products other than 1-aminoanthraquinone-2-sulphonic acid (see U. S. P. 1,841,997 and British Patent 289,097).

In carrying out the sulphonation process of the present invention, an amount of chlorsulphonic acid substantially equal to that required theoretically for monosulphonation of 1-aminoanthraquinone is preferably employed. While the use of less than an equimolecular amount of chlorsulphonic acid results merely in undersulphonation of 1-aminoanthraquinone and does not diminish the yield of 1-aminoanthraquinone-2-sulphonic acid obtained (based on the consumed 1-aminoanthraquinone), the use of chlorsulphonic acid in amounts materially (i. e., more than 15 per cent) in excess of an equimolecular amount is preferably avoided since it results in the production of increased amounts of by-products with diminution in yield of 1-aminoanthraquinone-2-sulphonic acid.

The present invention provides a means for the commercial production of 1-aminoanthraquinone-2-sulphonic acid free from the disadvantages of the previously proposed processes. Thus, 1-aminoanthraquinone-2-sulphonic acid of excellent quality is obtained in high yields (based on the weight of the 1-aminoanthraquinone consumed). The process also has a number of practical advantages over the prior art processes, particularly those involving the use of inert organic solvents. Thus, inert organic solvents are more expensive than sulphuric acid monohydrate; they must be recovered by distillation, thereby adding to the capital outlay and operating costs; and they have to be used in much greater amount, thereby producing a smaller quantity of useful product per unit volume of reaction mass. Furthermore, in the case of processes employing an inert organic solvent such as the process set forth in Example 1 of U. S. P. 2,135,346, the sulphonation mass thickens during the reaction to such an extent that agitation of the reaction mass and completion of the reaction becomes extremely difficult unless unusually powerful agitation is applied, in spite of the fact that the reaction mass is held at 150° to 155° C. during the latter part of the reaction. On the other hand, in the process of the present invention, the reaction mass remains fluid and readily agitated at temperatures down to about 110° C., even though containing a much greater initial charge of 1-aminoanthraquinone per unit volume of the reaction mass than in the process of Example 1 of U. S. P. 2,135,346.

In accordance with the process of the present invention the reaction will take place at a substantially lower temperature than that required by most of the prior art, uniform heat control throughout the entire reaction mass is readily obtained, and no alkali metal sulphates or other foreign materials need be present during the reaction. In fact, it has been found that the presence of alkali metal sulphates is detrimental and reduces the yield of the process.

The following examples illustrate the process of the present invention. The parts are by weight and the temperatures are in degrees centigrade.

Example 1.—150 parts of 100 per cent sulphuric acid are heated to 130° to 135° and agitated, and 150 parts of 1-aminoanthraquinone are added to it as rapidly as agitation permits. The mixture is agitated at that temperature until

a complete solution is obtained. Into the resulting solution, 78 parts of chlorsulphonic acid are stirred at a uniform rate over a period of about 3 hours, during which the temperature of the reaction mass is maintained at 130° to 135°. After the addition of chlorsulphonic acid is complete, the reaction mass is agitated for an additional 10 minutes at 130° to 135° and is then poured into 500 parts of cold water. The resulting aqueous mass is further diluted with 1500 parts of water, and neutralized with 305 parts of a 50 per cent solution of sodium hydroxide in water. The agitated batch is heated to 90°, 200 parts of common salt are stirred in, and the agitated mass is then cooled to 80° and filtered. The filter-cake, consisting essentially of 1-aminoanthraquinone-2-sodium sulphonate and unreacted 1-aminoanthraquinone, is slurried with 2000 parts of water, the slurry is heated to boiling to dissolve the 1-aminoanthraquinone-2-sodium sulphonate and then filtered, and the filter-cake is washed with hot water until a colorless filtrate is obtained, to remove adhering filtrate. The resulting filter-cake, when dried, weighs about 49 parts; it is essentially unreacted 1-aminoanthraquinone which is suitable for use in succeeding sulphonations. The filtrate, together with the wash waters, is heated to boiling. To the hot liquid, 20 per cent of its weight of common salt is added to precipitate the sodium salt of 1-aminoanthraquinone-2-sulphonic acid. After being cooled to 80°, the batch is filtered, and the filter-cake of 1-aminoanthraquinone-2-sodium sulphonate is washed with 1665 parts of a hot (85°) 15 per cent solution of common salt in water, and then dried. 165.5 parts of dry product are obtained, containing 143 parts of 1-aminoanthraquinone-2-sodium sulphonate in admixture with inorganic salts (e. g., sodium chloride and sodium sulphate), which correspond to about 98 per cent of the theoretical yield of the sulphonate, on the basis of the amount of 1-aminoanthraquinone consumed.

Example 2.—223 parts of 1-aminoanthraquinone are added to 450 parts of agitated 100 per cent sulphuric acid which is at atmospheric temperature. To this mixture, while continuously agitated, 110 parts of chlorsulphonic acid are added and the mass is then gradually heated to a temperature of about 135° to about 145°, and maintained there for about 16 hours. The batch is then poured into 2000 parts of cold water, neutralized to faint alkalinity on brom-cresol green indicator paper with a 50 per cent solution of sodium hydroxide in water, and heated to about 85° to 90°. To the hot, agitated liquid, 450 parts of common salt are added, and the resulting slurry is filtered. The filter-cake, which contains the sodium salt of 1-aminoanthraquinone-2-sulphonic acid and unreacted 1-aminoanthraquinone, is added to 2000 parts water, and the aqueous mixture is heated to boiling and then filtered. The filter-cake, consisting of the unsulphonated 1-aminoanthraquinone, is washed with about 1000 parts of boiling water, to remove adhering filtrate, and the wash waters are added to the filtrate. (The remaining filter-cake of unsulphonated 1-aminoanthraquinone, when dried, weighs 64 parts.) To the combined filtrate and wash waters common salt is added until the liquid is substantially a 10 per cent brine solution, whereby 1-aminoanthraquinone-2-sodium sulphonate is precipitated. The slurry is heated to between 85° and 90° and filtered. The filter-cake

is dried in an air oven at about 100°. 230 parts of dry cake containing 196 parts of 1-aminoanthraquinone-2-sodium sulphonate are obtained, which represent a yield of 84.5% of the theoretical yield (based on the weight of 1-aminoanthraquinone consumed).

It will be realized by those skilled in the art that the invention is not limited to the details of the above examples and that changes can be made without departing from the scope of the invention.

The 1-aminoanthraquinone-2-sulphonic acid may be recovered from the sulphonation mass in any suitable manner, although the method set forth in the above examples is preferred. For example, the mass may be diluted with water, preferably in amounts of from about 2 to about 10 times the weight of the sulphonation mixture; then the aqueous mass may be neutralized with a suitable base, for example, sodium hydroxide or sodium carbonate; the aqueous neutralized sulphonation mass may be salted, preferably with an amount of common salt sufficient to raise the total inorganic salt content to about 15 to 20 per cent of the weight of the liquid mass, to precipitate the sodium salt of 1-aminoanthraquinone-2-sulphonic acid; the batch may be filtered, preferably at a temperature above about 80° C.; the filter-cake washed free from acid, if necessary, with brine containing at least 15 per cent of salt; the filter-cake may then be slurried with about 2 to 10 times its weight of water to dissolve all water-soluble constituents thereof; and the hot slurry filtered, preferably at the boil. The filter-cake so obtained consists essentially of unreacted 1-aminoanthraquinone. Instead of neutralizing and salting the sulphonation mass in the aforesaid manner to precipitate the sodium salt of 1-aminoanthraquinone-2-sulphonic acid, this salt may be precipitated directly from the diluted acid sulphonation mass by adding thereto common salt in an amount equal to about 20 per cent of the weight of the liquid mass.

The filtrate may be salted, preferably with at least 20 per cent of its weight of common salt, to precipitate the sodium salt of 1-aminoanthraquinone-2-sulphonic acid, and the latter may be conveniently recovered as a filter-cake by filtering the slurry, preferably at a temperature above about 80° C. in order to retain dissolved in the mother liquor as much as possible of impurities, which at lower temperatures, particularly at about 60° C., tend to precipitate.

In place of the 1-aminoanthraquinone of the examples, there may be employed other alpha-aminoanthraquinone compounds in which the 2-, 3-, and 4-positions are unsubstituted while one or more of the positions 5, 6, 7 and 8 may be substituted, for example by halogen or an amino or sulphonic acid group. Examples of such substituted aminoanthraquinone compounds are: 1-amino-5 (6, 7 or 8)-chloranthraquinone; 1-aminoanthraquinone-5-sodium sulphonate; 1,5- or 1,8-diaminoanthraquinone, etc. Thus, by the process of the present invention 1,5-diaminoanthraquinone can be sulphonated in one stage to form 1,5-diamino-2-sulphoanthraquinone and then the latter compound may be treated to form 1,5-diamino-2,6-disulphoanthraquinone.

Since, in carrying out the above process, changes may be made in the ingredients, procedure and conditions employed without departing from the scope of the invention, it is intended that all matter contained in the above descrip-

tion shall be interpreted as illustrative and not in a limiting sense, except as limited by the claims.

I claim:

1. In the process for the preparation of a 1-aminoanthraquinone-2-sulphonic acid compound by sulphonating an aminoanthraquinone compound in which the amino group is in the 1-position and the 2-, 3-, and 4-positions are unsubstituted, the improvement which comprises sulphonating said aminoanthraquinone compound with chloresulphonic acid in the presence of sulphuric acid monohydrate as the reaction medium.

2. In the process for the preparation of a 1-aminoanthraquinone-2-sulphonic acid compound by sulphonating an aminoanthraquinone compound in which the amino group is in the 1-position and the 2-, 3-, and 4-positions are unsubstituted, the improvement which comprises sulphonating said aminoanthraquinone compound with about an equimolecular quantity of chloresulphonic acid in the presence of sulphuric acid monohydrate as the reaction medium.

3. In the process for the preparation of a 1-aminoanthraquinone-2-sulphonic acid compound by sulphonating an aminoanthraquinone compound in which the amino group is in the 1-position and the 2-, 3-, and 4-positions are unsubstituted, the improvement which comprises sulphonating said aminoanthraquinone compound with chloresulphonic acid in the presence of less than 4 parts of sulphuric acid monohydrate for each part by weight of aminoanthraquinone compound, as the reaction medium.

4. In the process for the preparation of a 1-aminoanthraquinone-2-sulphonic acid compound by sulphonating an aminoanthraquinone compound in which the amino group is in the 1-position, the 2-, 3-, and 4-positions are unsubstituted and the 5-, 6-, 7-, and 8-positions are occupied by members selected from the group consisting of hydrogen, amino, halogen and sulphonic acid, the improvement which comprises reacting said aminoanthraquinone compound with about an equimolecular quantity of chloresulphonic acid in the presence of less than 4 parts of sulphuric acid monohydrate for each part by weight of aminoanthraquinone compound, as the reaction medium, at a temperature of 120° to 160° C.

5. In the process for the preparation of a 1-aminoanthraquinone-2-sulphonic acid compound by sulphonating an aminoanthraquinone compound in which the amino group is in the 1-position and the 2-, 3-, and 4-positions are unsubstituted, the improvement which comprises reacting said aminoanthraquinone compound with chloresulphonic acid in the presence of from 0.8 to 2 parts of sulphuric acid monohydrate, for each part by weight of aminoanthraquinone compound, as the reaction medium, at a temperature of 120° to 160° C.

6. In the process for the preparation of a 1-aminoanthraquinone-2-sulphonic acid compound by sulphonating an aminoanthraquinone compound in which the amino group is in the 1-position and the 2-, 3-, and 4-positions are unsubstituted, the improvement which comprises adding chloresulphonic acid to said aminoanthraquinone compound contained in sulphuric acid monohydrate as a reaction medium while maintaining the mixture at a sulphonation temperature.

7. In the process for the preparation of a 1-aminoanthraquinone-2-sulphonic acid compound by sulphonating an aminoanthraquinone com-

pound in which the amino group is in the 1-position and the 2-, 3-, and 4-positions are unsubstituted, the improvement which comprises adding chlorsulphonic acid to a mixture of said aminoanthraquinone compound with 0.8 to 4 times its weight of sulphuric acid monohydrate as a reaction medium while maintaining the temperature of the mixture at 120° to 160° C.

8. In the process for the preparation of a 1-aminoanthraquinone-2-sulphonic acid compound by sulphonating an aminoanthraquinone compound in which the amino group is in the 1-position and the 2-, 3-, and 4-positions are unsubstituted, the improvement which comprises gradually adding chlorsulphonic acid to a solution of said aminoanthraquinone compound in less than 4 times its weight of sulphuric acid monohydrate as a reaction medium while maintaining the solution at a sulphonation temperature, the amount of chlorsulphonic acid being about an equimolecular amount, based on the aminoanthraquinone compound.

9. In the process for the preparation of 1-aminoanthraquinone-2-sulphonic acid by sulphonating 1-aminoanthraquinone, the improvement which comprises reacting chlorsulphonic acid with 1-aminoanthraquinone at a sulphonation temperature and in the presence of sulphuric acid monohydrate as the reaction medium.

10. In the process for the preparation of 1-aminoanthraquinone-2-sulphonic acid by sulphonating 1-aminoanthraquinone, the improvement which comprises heating chlorsulphonic acid with 1-aminoanthraquinone in less than 4 parts of sulphuric acid monohydrate for each part by weight of 1-aminoanthraquinone, as the reaction medium.

11. In the process for the preparation of 1-aminoanthraquinone-2-sulphonic acid by sulphonating 1-aminoanthraquinone, the improvement which comprises reacting chlorsulphonic acid with about an equimolecular quantity of 1-aminoanthraquinone in 0.8 to 2 parts of sulphuric acid monohydrate for each part by weight of 1-aminoanthraquinone, as the reaction medium, at a temperature of 120° to 160° C.

12. The process for the preparation of 1-aminoanthraquinone-2-sulphonic acid by sulphonating 1-aminoanthraquinone which comprises heating about 1 part of 1-aminoanthraquinone in less than 4 parts by weight of sulphuric acid monohydrate to a temperature of 120° to 160° C., and adding to the resulting mixture about an equi-

molecular quantity of chlorsulphonic acid, based on the aminoanthraquinone, in portions at about the same rate as it is consumed in the reaction.

13. The process for the preparation of 1-aminoanthraquinone-2-sulphonic acid by sulphonating 1-aminoanthraquinone which comprises heating about 1 part of 1-aminoanthraquinone in about 1 part by weight of sulphuric acid monohydrate to a temperature of 120° to 160° C., and adding to the resulting solution about an equimolecular quantity of chlorsulphonic acid, based on the aminoanthraquinone, in portions at about the same rate as it is consumed in the reaction.

14. The process for the preparation of 1-aminoanthraquinone-2-sulphonic acid by sulphonating 1-aminoanthraquinone which comprises adding about an equimolecular quantity of chlorsulphonic acid, based on the 1-aminoanthraquinone, during about 3 hours to a mixture of about equal parts by weight of 1-aminoanthraquinone and sulphuric acid monohydrate which has been heated to a temperature of 130° to 140° C. while maintaining the said temperature.

15. The process for the preparation of 1-aminoanthraquinone-2-sulphonic acid by sulphonating 1-aminoanthraquinone which comprises adding about an equimolecular quantity of chlorsulphonic acid, based on the 1-aminoanthraquinone, to a solution of 1-aminoanthraquinone in about an equal part by weight of sulphuric acid monohydrate while maintaining the solution at a temperature of 130° to 140° C.

16. The process for the preparation of 1-aminoanthraquinone-2-sulphonic acid by sulphonating 1-aminoanthraquinone which comprises dissolving 1 part of 1-aminoanthraquinone in about 1 part of sulphuric acid monohydrate while agitating and heating the solution to 130° to 135° C., then adding about an equimolecular quantity of chlorsulphonic acid, based on the 1-aminoanthraquinone, at a uniform rate over a period of about three hours while maintaining the temperature at 130° to 135° C., maintaining the temperature of the reaction mass at 130° to 135° C. for a short period of time after the addition of the chlorsulphonic acid is completed, drowning the reaction mass in cold water, neutralizing the resulting solution, separating unreacted 1-aminoanthraquinone from the remaining solution, and salting out and recovering the sodium salt of 1-aminoanthraquinone-2-sulphonic acid from said solution.

JAMES OGILVIE.