

# PATENT SPECIFICATION

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## (54) PROCESS FOR THE PREPARATION OF 1-AMINO-8-NAPHTHOL-3,6-DISULPHONIC ACID (H-ACID)

(71) We, BAYER AKTIENGESSELLSCHAFT, a body corporate organised under the laws of Federal Republic of Germany of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the preparation of 1 - amino - 8 - naphthol - 3,6 - disulphonic acid (H-acid), as the mono-alkali metal salt, from naphthylamine-trisulphonic acid isomer mixtures by alkaline hydrolysis under pressure.

1 - Amino - 8 - naphthol - 3,6 - disulphonic acid, which is frequently also designated H-acid, is an important intermediate product for the preparation of dyestuffs (see Ullmanns Enzyklopädie der Technischen Chemie (Ullmann's Encyclopaedia of Industrial Chemistry), 3rd edition, volume 12, page 621).

It is known from FIAT Final Report No. 1,016, page 32 to 39, that H-acid can be prepared as follows: naphthalene is reacted with sulphuric acid monohydrate (= 100% strength H<sub>2</sub>SO<sub>4</sub>) and 65% strength oleum, whilst maintaining a particular temperature programme and stepwise addition of sulphuric acid mono-hydrate and oleum, to give a naphthalene-trisulphonic acid isomer mixture which is nitrated with mixed acid. After diluting with water, driving off the nitrous gases and separating off the sulphuric acid as calcium sulphate, the isomer mixture of the nitro - naphthalene - trisulphonic acids is reduced with iron and dissolved iron salts are then precipitated with magnesium oxide and separated off. The acid calcium sodium salt of T - acid (1 - naphthylamine - 3,6,8 - trisulphonic acid) is precipitated by adding rock salt and hydrochloric acid and is filtered off and washed several times. This salt is introduced into wash water and sodium carbonate

is added. The chalk which has precipitated is then pressed off and the salt solution is concentrated. The concentrated trisodium salt solution of T-acid is reacted with 50% strength sodium hydroxide solution under pressure. First sulphuric acid and then water are subsequently added, and the H-acid is finally obtained as the monosodium salt by filtration, washing and drying.

It is a disadvantage in this process that the T-acid must be separated off as the acid calcium sodium salt in an intermediate stage, an effluent being obtained which is extremely difficult and expensive to work up since it also contains, in addition to organic constituents, large amounts of sodium chloride, calcium chloride and hydrochloric acid. The salt of T-acid thus separated off also contains sodium chloride. This can only be washed out with loss of T-acid. If it is left in the T-acid, after separating off the chalk the solution can be concentrated no further than up to a concentration which corresponds, on titration of 100 g of solution, to a nitrite consumption of about 5.5 g, since otherwise salt deposits occur which do not permit a continuous procedure. However, a solution which is as concentrated as possible is desired for the subsequent reaction with sodium hydroxide solution in order to keep the amount of alkali required to set up a particular alkali concentration in the reaction mixture as low as possible.

It has now been discovered that the preparation of 1 - amino - 8 - naphthol - 3,6-disulphonic acid is significantly improved if the isolation of T-acid is omitted and instead of T-acid there is hydrolysed a mixture of isomeric naphthylamine trisulphonic acids and/or their salts.

According to the present invention a process has been found for the preparation of mono-alkali metal salts of 1 - amino - 8-naphthol - 3,6 - disulphonic acid, which is

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characterised in that a mixture of naphthylamine-trisulphonic acids and/or their salts is reacted with an alkali metal hydroxide solution under elevated pressure and at elevated temperature, and 1 - amino - 8 - naphthol-3,6 - disulphonic acid is then precipitated in the form of the mono-alkali metal salt by acidifying and is separated off.

5 Examples of a suitable feed product are naphthylamine-trisulphonic acid isomer mixtures which are obtained in the industrial preparation of T-acid. In general, mixtures which can be employed in the process according to the invention contain over 65% by weight of 10 1 - naphthylamine - 3,6,8 - trisulphonic acid (T-acid), relative to the total amount of diazotisable substances. These mixtures which contain 70 to 90% by weight of 1 - naphthylamine - 3,6,8 - trisulphonic acid are preferably employed. A naphthylaminetrisulphonic acid mixture which is to be particularly preferably employed contains 75 to 85% by weight of 1 - naphthylamine - 3,6,8 - trisulphonic acid, 5 to 15% by weight of 1 - naphthylamine - 3,5,7 - trisulphonic acid, 1 to 15% by weight of 1 - naphthylamine - 4,6,8-trisulphonic acid, 0.5 to 5% by weight of 1-naphthylamine - 2,5,7 - trisulphonic acid, 0.1 to 2% by weight of 2 - naphthylamine - 3,5,7-trisulphonic acid, 0.1 to 2% by weight of 2-naphthylamine - 4,6,8 - trisulphonic acid and 0.1 to 2% by weight of 2 - naphthylamine-3,6,8 - trisulphonic acid.

Such mixtures can be obtained, for example, 35 by trisulphonating naphthalene, nitrating the mixture formed and reducing the nitro-naphthalenetrisulphonic acid mixture then present. These reactions can be carried out by the procedure described initially according to FIAT 40 Final Report No. 16, page 37 to 38, or by any other desired manner.

The naphthylaminetrisulphonic acid mixture can contain the acids in the free form, 45 in the form of neutral salts or in the form of acid salts. Mixtures which contain free acids and salts can also be used. If some or all of the naphthylaminetrisulphonic acids are present as salts, the alkali metal salts and alkaline earth metal salts, in particular the sodium salts and potassium salts, are preferred. 50 Naphthylaminetrisulphonic acid mixtures which contain the acids in the form of trisodium salts are very particularly preferred.

In addition to the naphthylaminetrisulphonic acids or their salts, the naphthylaminetrisulphonic acid mixture can also contain further products. Such products can be, in particular, by-products, decomposition products or unreacted intermediate products from the preparation stages for naphthylaminetrisulphonic acid, for example naphthalene-di-, -tri- and -tetra-sulphonic acids, nitronaphthalene-mono-, -di- and -tri-sulphonic acids, naphthylamine-mono- and -di-sulphonic acids,

for example 1-naphthylamine-3,6- and -5,7-disulphonic acid, and furthermore dinaphthylsulphone-sulphonic acids and their amino and nitro derivatives, as well as oxidation products of naphthalene and/or of naphthalenesulphonic acids, which can be formed during the sulphonation and/or nitration. 65 70

The naphthylamine trisulphonic acid mixture can be employed in the solid form, or as an aqueous solution containing, for example, 20 to 50% by weight, preferably 30 to 40% by weight, calculated as the free acid with the molecular weight 383. 75

Possible alkali metal hydroxide solutions for the process according to the invention are, in particular aqueous potassium hydroxide solution or aqueous sodium hydroxide solution. Compared with sodium hydroxide solution, the use of potassium hydroxide solution leads to better yields, but in general sodium hydroxide solution is more favourable from the point of view of cost. 2.5 to 12 mols, for example, of alkali metal hydroxide can be employed per mol of diazotisable substance (calculated with a molecular weight of 383 = T-acid). It is particularly preferable to employ 6 to 9 mols of alkali metal hydroxide per mol of diazotisable substance. The concentration of alkali metal hydroxide in the reaction mixture can be, for example, 10 to 50% by weight (relative to the sum of alkali metal hydroxide + total water) This concentration is preferably 25 to 35% strength by weight. 80 85 90 95

The reaction can be carried out at temperatures from 150 to 250°C, preferably at 180 to 220°C, in a closed vessel. In general, the pressure which is thereby set up is completely sufficient for carrying out the process according to the invention in a satisfactory manner. It is also possible, of course, to carry out the process according to the invention under pressures other than those which are set up by themselves in the closed vessel. For example, pressures in the range from 5 to 50 bars are possible for the process according to the invention. 100 105 110

The reaction time essentially depends on the reaction temperature and the alkali metal hydroxide concentration. It is shorter at relatively high reaction temperatures and at relatively high alkali metal hydroxide concentrations and longer at relatively low reaction temperatures and relatively low alkali metal hydroxide concentrations and in general is 10 minutes to 10 hours. For example, good results are obtained in a reaction time of one hour at a reaction temperature of about 200°C and an alkali metal hydroxide concentration of 30% by weight. 115 120

When carrying out the process according to the invention it is essential that favourable concentrations of alkali metal hydroxide are present during the entire reaction. Thus the procedure is preferably to pump in the naph- 125

thylamine trisulphonic acid isomer mixture and most of the alkali metal hydroxide solution simultaneously into a small amount of alkali metal hydroxide solution in the course of, for example, 5 to 30 minutes, preferably 10 to 20 minutes, and then to allow the mixture to react completely. The starting substances are most appropriately introduced into the reaction vessel at a temperature such that the desired reaction temperature is present after the heat of mixing and, if appropriate, the heat of neutralisation have been liberated. The starting substances can also be brought together at relatively low temperatures and heated in the reaction vessel to the desired reaction temperature.

After the reaction has ended and before the H-acid is separated out as the mono-alkali metal salt, it is advantageous to cool the reaction mixture and/or to dilute it with water. It can be cooled, for example, to temperatures in the range of 20—150°C, preferably to temperatures in the range of 80—120°C. The amount of water to be optionally added depends on the reaction conditions, for example the nature of the alkali metal hydroxide and its amount and concentration. It is advantageous to choose the amount of water so that the alkali metal sulphite formed during the reaction is dissolved.

The H-acid can be separated out as the mono-alkali metal salt by acidifying the reaction mixture with mineral acids. Sulphuric acid is preferably used for this. Sufficient mineral acid is added for the sparingly soluble mono-alkali metal salt of H-acid to form. By correspondingly choosing the concentration of the mineral acid and/or by adding water before and/or during the addition of the mineral acid, it is appropriately ensured that the inorganic salt which forms, for example sodium sulphate or potassium sulphate, does not precipitate. It is possible, for example, to obtain good results if, in order to separate out the H-acid as the mono-alkali metal salt, the pH is adjusted to a value in the range from 0 to 4, preferably 0.5 to 2.5, and 0.1 to 5 times, preferably 0.5 to 2 times, the amount of water is incorporated, by dilution with water and/or by appropriately choosing the concentration of the mineral acid, relative to the weight of the mixture present in the hydrolysis reaction under pressure. The mono-alkali metal salt of H-acid can be separated off in the customary manner, for example by filtration. It is advantageous to adjust the temperature to less than 80°C by cooling, for example by evaporative cooling, before separating the mono-alkali metal salt of H-acid and to carry out the separation at a temperature of less than 80°C. The separation is preferably carried out at a temperature in the range from 20 to 60°C.

For complete removal of sulphur dioxide it

is advantageous, after setting up the precipitation conditions and before separating off the mono-alkali metal salt of H-acid, for the acidified and diluted mixture to be boiled under reflux or kept in vacuo for some time, for example 0.5 to 2 hours, or for the sulphur dioxide to be blown out with an inert gas, for example nitrogen.

The mono-alkali metal salt of H-acid present after the separation is usually washed with water and dried, for example in vacuo.

The mono-alkali metal salt of H-acid can be isolated in almost quantitative yield and very high purity (for example 98—99% relative to all the organic compounds present) by the process according to the invention.

This is very surprising since about 25 different components can be detected in the mixture present after the hydrolysis under pressure, and in particular the sparingly soluble W-acid (1 - amino - 6 - naphthol - 3,8 - disulphonic acid) is found in the isolated product in substantially smaller amounts than when pure T-acid or a pure salt of T-acid is employed (see Example 5).

Compared with the alkaline hydrolysis under pressure of precipitated T-acid, which was customary hitherto, the process according to the invention has considerable advantages and is therefore particularly economical. Thus, in the process according to the invention, the process stage for separating off and isolating the T-acid as the acid calcium sodium salt is omitted. The entire T-acid is utilised for the alkaline hydrolysis under pressure, so that an improved yield of H-acid, relative to naphthalene originally employed, results. Compared with the solution of the precipitated T-acid, which contains sodium chloride, the salt-free T-acid isomer mixture solution can be concentrated substantially more highly without salt deposits forming. For example, it is possible to concentrate the solution up to a concentration which corresponds, on titration of 100 g of solution, to a nitrite consumption of about 7.5 g. This results in a saving of alkali metal hydroxide, using the same concentration of alkali in the reaction mixture. Finally, effluent is obtained only once in the process according to the invention, namely during the separating out of the H-acid. In addition to organic compounds, this effluent contains only the inorganic salt formed during the neutralisation, for example sodium sulphate, and a little mineral acid, for example sulphuric acid. Compared with the process used hitherto, the total amounts of effluent and salt are very greatly reduced.

#### Example 1.

580 g of a naphthylaminetrisulphonic acid mixture, in the form of the trisodium salts (content: 11.9 g of total nitrite/100 g, 52.8% by weight of T-acid, MW 383; a total of

69 g of nitrite, 0.80 mol of T-acid) of the following composition: 80.0% of 1 - naphthylamine - 3,6,8 - trisulphonic acid, 8.5% of 1 - naphthylamine - 3,5,7 - trisulphonic acid, 4.0% of 1 - naphthylamine - 4,6,8 - trisulphonic acid, 3.0% of 1 - naphthylamine - 2,5,7 - trisulphonic acid, 1.2% of 2 - naphthylamine - 3,5,7 - trisulphonic acid, 0.7% of 2 - naphthylamine - 4,6,8 - trisulphonic acid and 0.5% of 2 - naphthylamine - 3,6,8 - trisulphonic acid (the contents in % are in each case relative to diazotisable substance), which additionally contains 0.3% by weight of the disodium salt of 1 - naphthylamine - 3,6 - disulphonic acid, 1.3% by weight of the trisodium salt of naphthalene - 1,3,6 - trisulphonic acid, 0.6% by weight of the trisodium salt of 1 - nitronaphthalene - 3,6,8 - trisulphonic acid, 4.6% by weight of water and amounts of amino and nitro derivatives of dinaphthyl - sulphone - sulphonic acid and of oxidation products of naphthalene and of naphthalene - trisulphonic acids which cannot be determined quantitatively, and 400 g of water are initially introduced into a 2.7 litre nickel autoclave and heated to 180°C. 600 g of 50% strength by weight sodium hydroxide solution (7.5 mols of NaOH) are heated to 185°C in a 1.3 litre steel autoclave and forced into the 2.7 litre autoclave with nitrogen, whereby a 30% strength by weight sodium hydroxide solution forms, relative to the total water. A temperature of 200°C is thereby set up. The reaction mixture is kept at 200°C for 45 minutes, cooled to 100°C as rapidly as possible and diluted with 500 g of water. The hot reaction solution is acidified with about 1,000 g of 50% strength by weight sulphuric

acid, controlling the pH (pH 1 to 1.5), and the mixture is heated under reflux for one hour to completely remove the sulphur dioxide, cooled to 40°C with evaporative cooling and kept at 40°C for 2 hours. The product is filtered off at 40°C, washed with a total of 500 g of water and dried at 80°C in vacuo.

The yield is 58%, relative to T-acid isomer mixture, or 72%, relative to T-acid. The quality of the H-acid was determined, by high pressure liquid chromatography, as follows: 88.2% of the monosodium salt of H-acid, 0.1—0.2% of the monosodium salt of 1 - naphthylamine - 3,6 - disulphonic acid, 0.1—0.2% of the monosodium salt of W-acid, 1.1—1.2% of the disodium salt of chromotropic acid, 0.1—0.2% of the disodium salt of T-acid, 9.0% of water and 0.5% of sodium sulphate.

The reaction products from the isomeric naphthylaminetrisulphonic acids are not contained in the isolated product.

#### Examples 2a to 2n.

The procedure followed was as in Example 1, but the following reaction parameters were varied:

1. Molar ratio of NaOH:T-acid isomer mixture, in the form of the trisodium salts
2. NaOH concentration, relative to the total water
3. Temperature
4. Reaction time

The results are summarised in Table 1.

TABLE 1

Example	Reaction conditions				Yield		Quality +) (contents)				
	Molar ratio of NaOH:T-acid isomer mixture (MW 383)	NaOH concentration, relative to water % by weight	Temperature °C	Time minutes	relative to T-acid isomer mixture %	relative to T-acid %	H-acid MW 319 %	1-naphthylamine-3,6-disulphonic acid MW 303 %	W-acid MW 319 %	Chromotropic acid MW 320 %	T-acid MW 383 %
2a	6:1	30	200	70	55	70	82.6	0.1	0.1	0.8	0.3
2b	7:1	30	220	18	57	72	81.6	0.1	0.2	1.4	0.1
2c	8:1	30	220	15	58	73	82.8	0.2	0.1	0.9	Ø
2d	9:1	30	220	13	57	72	81.9	0.1	0.1	0.9	0.1
2e	7.5:1	20	180	240	54	69	79.1	0.2	0.1	0.6	0.3
2f	7.5:1	25	200	50	56	71	83.2	0.1	0.1	1.0	0.2
2g	7.5:1	30	190	100	58	73	82.3	0.1	Ø	1.0	0.2
2h	7.5:1	35	190	90	57	72	83.2	0.2	Ø	0.8	0.1
2i	8.5:1	25	180	210	55	70	80.0	0.2	Ø	0.9	0.2
2k	8.5:1	25	190	110	57	72	82.4	0.2	0.1	1.3	0.3
2l	8.5:1	25	200	45	57	72	81.8	0.1	Ø	1.3	0.1
2m	8.5:1	25	210	25	58	73	81.4	0.1	Ø	0.7	0.2
2n	8.5:1	25	220	15	58	73	81.4	0.1	0.1	0.9	Ø

+) Virtually only water and 0.3 to 1.5% of sodium sulphate are also present to make up to 100%. The contents of the organic acids indicated are calculated with respect to free acids. In fact, these are present in the form of the salts indicated in Example 1.

### Example 3.

933 g of a T-acid isomer mixture, in the form of the tripotassium salts, (content: 11.1 g of nitrite/100 g, 48% by weight of T-acid, MW 383; a total of 103.5 g of nitrite, 1.17 mols of T-acid) of the following composition: 78.0% of 1-naphthylamine-3,6,8-trisulphonic acid, 8.0% of 1-naphthylamine-

3,5,7-trisulphonic acid, 3.9% of 1-naphthylamine-4,6,8-trisulphonic acid, 3.0% of 1-naphthylamine-2,5,7-trisulphonic acid, 1.1% of 2-naphthylamine-3,5,7-trisulphonic acid, 0.6% of 2-naphthylamine-4,6,8-trisulphonic acid and 0.4% of 2-naphthylamine-3,6,8-trisulphonic acid (contents in % are in each case relative to

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- 5 diazotisable substance) and 480 g of water are heated to 200°C in a 2.7 litre nickel autoclave. 360 g of 70% strength by weight potassium hydroxide solution (4.6 mols of KOH) at 210°C are forced in with nitrogen. A temperature of 220°C is thereby set up and a 30% strength by weight KOH solution results, relative to the total water. The reaction mixture is kept at 220°C for 27 minutes, cooled to 150°C in about 2 minutes by means of a cooling coil, and, after further cooling, is allowed to run into 3,000 g of hot water simultaneously with about 1,120 g of 50% strength by weight H<sub>2</sub>SO<sub>4</sub>, whilst controlling the pH at pH 1 to 1.5 and at 100 to 110°C. The reaction mixture is stirred at 100 to 110°C for two hours to remove sulphur dioxide, cooled to 40°C, with evaporative cooling, and kept at 40°C for one hour. The product is filtered off, washed with a total of 600 g of water and dried at 80°C in vacuo. The yield is 58%, relative to T-acid isomer mixture, or 74%, relative to T-acid.
- 15 Content: 88.3% of the monopotassium salt of H-acid, 8% of the monopotassium salt of W-acid, 0.7% of the dipotassium salt of chromotropic acid, 0.4% of the dipotassium salt of T-acid, 8.5% of water and 1.8% of potassium sulphate.
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- 30 Examples 4a to 4n.  
The procedure followed was as in Example 3, but the following reaction parameters were varied:
1. Molar ratio of KOH:T-acid isomer mixture, in the form of tripotassium salts 35
  2. KOH concentration, relative to the total water
  3. Temperature
  4. Reaction time
- The results are summarised in Table 2. 40
- Example 5.  
(comparison example)
- A reaction carried out as in Example 1, but using the pure trisodium salt of T-acid, gives a yield of 73%, but an increased content of W-acid and T-acid. 45
- Content: 88.6% of the monosodium salt of H-acid, 0.2% of the monosodium salt of 1-naphthylamine - 3,6 - disulphonic acid, 2.0% of the monosodium salt of W-acid, 1.4% of the disodium salt of chromotropic acid, 0.6% of the disodium salt of T-acid, 6.8% of water and 0.6% of sodium sulphate. 50
- Example 6.
- A reaction carried out as in Example 1, using a T-acid isomer mixture in the form of the calcium salt, gives a yield of 48%, relative to T-acid isomer mixture, or 60%, relative to T-acid. In this case, the calcium sulphite must be separated off by filtration before separating out the H-acid with sulphuric acid. 55
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TABLE 2

Example.	Reaction conditions				Yield		Quality +) (contents)				
	Molar ratio of KOH:T-acid isomer mixture (MW 383)	KOH concentration, relative to water % by weight	Temperature °C	Time minutes	relative to T-acid isomer mixture %	relative to T-acid %	H-acid MW 319 %	1-naphthyl-amine-3,6-disulphonic acid MW 303 %	W-acid MW 319 %	Chromotropic acid MW 320 %	T-acid MW 383 %
4a	3.5:1	30	200	120	58	75	77.7	Ø	Ø	1.0	0.5
4b	4:1	30	220	30	62	80	78.2	Ø	Ø	1.8	0.2
4c	5:1	25	220	30	63	81	75.8	Ø	Ø	1.5	0.4
4d	6:1	30	220	28	64	82	81.2	Ø	Ø	Ø	Ø
4e	8:1	30	220	22	63	81	80.4	Ø	Ø	0.5	0.2
4f	5:1	20	200	180	62	80	75.8	Ø	Ø	2.6	0.6
4g	3.5:1	25	220	55	57	74	77.2	Ø	Ø	2.0	0.1
4h	3.5:1	30	220	30	59	76	79.4	Ø	Ø	0.4	0.3
4i	3:1	35	220	30	57	74	75.3	Ø	Ø	1.6	0.2
4k	6:1	30	190	165	62	80	78.3	Ø	Ø	0.2	0.1
4l	6:1	30	200	80	62	80	79.8	Ø	Ø	0.4	Ø
4m	3.5:1	30	210	60	60	78	77.0	Ø	Ø	0.7	Ø
4n	3.5:1	25	220	55	57	74	78.1	Ø	Ø	0.8	0.4

+) Virtually only water and 0.5 to 2.0% of potassium sulphate are also present to make up to 100%. The contents of the organic acids indicated are calculated with respect to free acids. In fact, these are present in the form of the salts indicated in Example 3.

#### Example 7.

10.5 kg of a T-acid isomer mixture, in the form of dissolved trisodium salts, of the composition indicated in Example 1 (content: 6.9 g of nitrite/100 g, 31% by weight of T-acid, MW 383; a total of 724 g of nitrite, 8.5 mols of T-acid) and 4.65 kg of 70% strength by weight sodium hydroxide solution (81.5 mols of NaOH) are pumped simultaneously, in the course of 10 minutes and at 200°C, into a 20 litre nickel autoclave in which 0.4 kg of 30% strength by weight sodium hydroxide solution has been initially introduced. The reaction mixture is kept at 200°C for 40 15

minutes and then let down, in the course of about 5 minutes, into a 25 litre V4A kettle, into which 11.8 kg of cold water have been initially introduced. The dilute H-acid isomer mixture solution is forced with nitrogen, in the course of 40 to 60 minutes, into a glass precipitation vessel into which about 4 kg of water (or wash water from the initial batch) has been initially introduced. The pH value is kept at 1 to 1.5 by simultaneously running in about 5.2 kg of sulphuric acid monohydrate and the reaction mixture is brought to the boil. The hot, acid H-acid suspension is freed from residual sulphur dioxide by applying a vacuum, cooled to 40°C in the course of one hour, kept at 40°C for one hour and filtered. The product is washed with a total of 5.4 kg of water and dried at 80°C in vacuo. The yield is 61%, relative to T-acid isomer mixture, of 76%, relative to T-acid.

Content: 88.0% of the monosodium salt of H-acid, 0.2% of the monosodium salt of 1-naphthylamine - 3,6 - disulphonic acid, 0 of the monosodium salt of W-acid, 0.7% of the disodium salt of chromotropic acid, 0.1% of the disodium salt of T-acid, 2.0% of sodium sulphate and 9.4% of water.

#### Examples 8a to 8e.

The procedure followed was as in Example 7, but the following reaction parameters were varied:

1. Metering time
2. NaOH concentration, relative to the total water
3. Temperature
4. Subsequent stirring time

The results are summarised in Table 3.

#### Example 9.

5,945 kg of a T-acid isomer mixture of the following composition 82.1% of 1 - naphthylamine - 3,6,8 - trisulphonic acid, 6.8% of 1-naphthylamine - 3,5,7 - trisulphonic acid, 4.2% of 1 - naphthylamine 4,6,8 - trisulphonic acid, 2.9% of 1 - naphthylamine - 2,5,7 - trisulphonic acid, 0.8% of 2 - naphthylamine-3,5,7 - trisulphonic acid, 0.8% of 2 - naphthylamine - 4,6,8 - trisulphonic acid and 0.4% of 2 - naphthylamine - 3,6,8 - trisulphonic acid (contents in % are in each case relative to diazotisable substance), in the form of dissolved trisodium salts, with a content of 6.22 g of nitrite/100 g (a total of 370 kg of nitrite, 4.4 kmols of T-acid) and 3,170 kg of 50% strength by weight sodium hydroxide solution (a total of 39.6 kmols of NaOH) are forced simultaneously, with nitrogen, at 190°C in the course of about 17 minutes, into a 8 m<sup>3</sup> melting pot, into which 200 kg of 30% strength by weight sodium hydroxide solution have been initially introduced. The reaction mixture is kept at 190°C for 90 minutes and let down in the course of 15 to 30 minutes. The H-acid isomer mixture solution is allowed to run into 5,500 kg of 48% strength by weight sulphuric acid and 5,200 kg of water, and the H-acid is isolated in the customary manner. The yield is 60%, relative to T-acid isomer mixture, or 73%, relative to T-acid.

Content: 88.2% of the monosodium salt of H-acid, 0.1% of the monosodium salt of 1-naphthylamine - 3,6 - disulphonic acid, 0 of the monosodium salt of W-acid, 1.0% of the disodium salt of chromotropic acid, 0.5% of the disodium salt of T-acid, 1.5% of sodium sulphate and 9.9% of water.



TABLE 3

Example	Reaction conditions				Yield		Quality +) (contents)				
	NaOH con- centration, relative to the total water % by weight	Temperature °C	Metering time minutes	Sub- sequent stirring time minutes	relative to T-acid isomer mixture %	relative to T-acid %	H-acid MW 319 %	1-naphthyl- amine-3,6- disulphonic acid MW 303 %	W-acid MW 319 %	Chromotropic acid MW 320 %	T-acid MW 383 %
8a	25.5	200	10	60	58	73	83.7	0.2	Ø	0.8	0.4
8b	25.5	200	15	55	58	73	83.2	0.2	Ø	1.0	0.3
8c	25.5	200	20	50	58	73	82.6	0.2	Ø	1.0	0.2
8d	30	190	10	90	58	73	82.3	0.1	Ø	0.7	0.2
8e	35	190	10	80	59	74	81.4	0.2	Ø	0.4	0.2

<sup>†)</sup> Virtually only water and 0.3 to 1.5% of sodium sulphate are also present to make up to 100%. The contents of the organic acids indicated are calculated with respect to free acids. In fact, these are present in the form of the salts indicated in Example 7.

#### WHAT WE CLAIM IS:—

1. A process for the production of a mono-alkali metal salt of 1 - amino - 8 - naphthol-3,6 - disulphonic acid, in which a mixture of naphthylaminetrisulphonic acids and/or their salts is reacted with an alkali metal hydroxide solution under elevated pressure and at elevated temperature, and 1 - amino - 8 - naphthol - 3,6 - disulphonic acid is then precipitated in the form of mono-alkali metal salt by acidifying and is separated off.
2. A process according to claim 1, in which the reaction is carried out under a pressure in the range from 5 to 50 bars.
3. A process according to claim 1 or 2, in which the reaction is carried out at temperatures in the range from 150 to 250°C.
4. A process according to claim 3, in which the reaction is carried out at a temperature in the range from 180 to 220°C.
5. A process according to any of the foregoing claims, in which a mixture of naphthylaminetrisulphonic acids and/or their salts which contains over 65% by weight of 1-naphthylamine - 3,6,8 - trisulphonic acid, relative to the total amount of diazotisable substances, is employed.
6. A process according to claim 5, in which the mixture of naphthylaminetrisulphonic acids and/or their salts contain 70 to 90% by weight of 1 - naphthylamine - 3,6,8 - trisulphonic acid, relative to the total amount of diazotisable substances.
7. A process according to claim 6, in which the naphthylaminetrisulphonic acids mixture contains 75 to 85% by weight of 1 - naph-

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- thylamine - 3,6,8 - trisulphonic acid, 5 to 15% by weight of 1 - naphthylamine - 3,5,7 - trisulphonic acid, 1 to 10% by weight of 1 - naphthylamine - 4,6,8 - trisulphonic acid, 0.5 to 5% by weight of 1 - naphthylamine - 2,5,7 - trisulphonic acid, 0.1 to 2% by weight of 2 - naphthylamine - 3,5,7 - trisulphonic acid, 0.1 to 2% by weight of 2 - naphthylamine - 4,6,8 - trisulphonic acid, and 0.1 to 2% by weight of 2 - naphthylamine - 3,6,8 - trisulphonic acid.
8. A process according to any of the foregoing claims, in which a mixture of naphthylaminetrisulphonic acids in the form of their alkali metal salts or alkaline earth metal salts is used.
9. A process according to any of the foregoing claims, in which the reaction is carried out in 10 to 50% strength by weight aqueous alkali metal hydroxide solution, relative to the sum of alkali metal hydroxide plus total water.
10. A process according to claim 9, in which the reaction is carried out in 25 to 35% strength by weight aqueous alkali metal hydroxide solution, relative to the sum of alkali metal hydroxide plus total water.
11. A process according to any of the foregoing claims, in which 2.5 to 12 mols of alkali metal hydroxide are employed per mol of diazotisable substance.
12. A process according to any of the foregoing claims, in which 6 to 9 mols of alkali metal hydroxide are employed per mol of diazotisable substance.
13. A process according to any of the foregoing claims, in which, in order to separate out the mono-alkali metal salt of 1 - amino-8 - naphthol - 3,6 - disulphonic acid, the pH is adjusted to a value in the range from 0 to 4 with mineral acids and from 0.1 to 5 times the amount of water, relative to the weight of the mixture present in the hydrolysis reaction under pressure, is introduced.
14. A process according to claim 13, in which the pH is adjusted to 0.5 to 2.5 and 0.5 to 2 times the amount of water, relative to the weight of the mixture present in the hydrolysis reaction under pressure, is introduced.
15. A process according to any of the foregoing claims, in which the mixture is cooled to temperatures of less than 80°C. before separating off the mono-alkali metal salt of 1 - amino - 8 - naphthol - 3,6 - disulphonic acid.
16. A process according to claim 1, when carried out substantially as described in any one of Examples 1 to 4 and 6 to 9.
17. A mono-alkali metal salt of 1 - amino-8 - naphthol - 3,6 - disulphonic acid when produced by the process of any of the foregoing claims.

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