

ALIEN PROPERTY CUSTODIAN

DYESTUFFS DERIVED FROM THE 2-AMINO-3-NAPHTHOIC ACID, THEIR METHOD OF MANUFACTURE AND THEIR APPLICATIONS

Georges Kopp and René Eugène Marcel Gangneux, Rouen, France; vested in the Alien Property Custodian

No Drawing. Application filed April 5, 1940

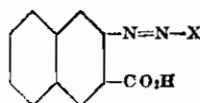
This invention relates to dyestuffs derived from the 2-amino-3-naphtoic acid, their method of manufacture and their applications.

While the anthranilic acid and its derivatives have been used frequently for the production of ortho-carboxy-ortho'-oxy- or -amino-azodyes for animal fibres, the 2-amino-3-naphtoic acid and its sulphonated derivatives have never been used for this application. The only technical dyestuffs which have been produced hitherto by means of the said products as diazotable bases have been dyestuffs for cellulosic fibres derived from the urea from the J-acid or dyestuffs for acetate rayon silks formed on the fibre.

Now, it has been found according to the present invention that azodyes of a great technical interest are obtained by diazotation of the 2-amino-3-naphtoic acid and its sulphonated derivatives and copulation in substance of the so obtained diazo compounds with copulation components copulating in ortho of a group NH² or OH with the exception of the derivatives of the 2-amino-5-naphtol-7-sulphonic acid. The so obtained dyestuffs can be converted in substance or on the fibre into metalliferous complexes.

The dyestuffs which form the subject matter of the present specification can be considered as falling into three categories:

I. Dyestuffs of the general formula:



in which X represents a copulating agent meeting the preceding definition and which may be, for example: an arylid of the acetylacetic acid, a betadiketone, a pyrazolone, a phenol, a naph-
 40 tol, a benzenic diamine, a naphthylamine, an aminonaphtol and other similar compounds. These products are little or not soluble in wa-

ter; after their conversion—by means of the known general methods—into metalliferous complexes such as those of chromium, nickel, cobalt, iron or copper, they possess remarkable solubilities in organic solvents (other than pure hydrocarbons) and in cellulosic varnishes.

These metalliferous dyestuffs which are solid to light, to sublimation and to setting off, form a scale going from yellow-green to purple and brown. They give excellent results in the coloration of varnishes and paints as well as in the coloration in the mass or body of films and rayon silks on the basis of esterified cellulose.

II. Sulphonated derivatives of the dyestuffs of the above general formula "I".—These dyestuffs are well soluble in water and lend themselves to the various usual tinctorial methods. But their generally poor solidity to fulling does not permit to use them as such.

On the contrary, when dyes obtained by means of these products are subsequently treated with a polyvalent metal salt able to form complexes, the said dyes acquire a series of very interesting properties.

The scale of the so obtained shades goes from yellow-green to blue and brown. These products show a remarkable affinity for leather which they permit readily to dye in well united generally bright shades with a good yield.

Certain of them can also be used in the manufacture of lacquers through precipitation by means of alkaline-earth salts; these lacquers are solid to light.

It is to be noted that the use of the 2-3-amino-naphtoic acid and of its sulphonated derivatives in the above mentioned conditions permits to obtain, through copulation by means of the usual methods with the arylids of the acetylacetic acid, very greenish yellows which it was hitherto impossible to obtain in this category of dyes with so simple components.

The dyestuffs of this category can be obtained when starting from components containing sulphonic groups, or by sulphonation of dyestuffs corresponding to the formula "I".

III. Metalliferous complexes of the dyestuffs of the above mentioned category "II".—The dyestuffs of the category "II" can be converted into metalliferous complexes. The so obtained novel products and more particularly the chromiferous complexes are very interesting as well from the point of view of their shades and of their brightness as from the point of view of their general properties: unison, light, fulling.

Like the di-ortho-oxyazodyes (see The U. S. Patent 2,133,864 of the 12th Nov. 1934) the novel dyestuffs of the category "II" lead to two kinds of chromiferous products, the ones preferably being formed in a neutral medium and the others exclusively in a strongly acid medium.

The differences of properties between the complexes formed in a neutral medium (primary complexes) and the complexes formed in an acid medium are generally very strongly marked. In most cases the secondary complexes are brighter and unite very well on wool in an acid bath while the primary complexes unite badly.

Furthermore, the primary complexes require large quantities of acid and very long dyeing periods while the secondary complexes can be readily dyed by the usual methods; an advantage of the primary complexes lies, again, in their better yield when dyeing on wool in a strongly acid bath.

The production of the secondary compounds and their separation from the reaction media are generally very simple; it is sufficient, for example, to heat the dyestuff with a chromium salt in a diluted sulphuric medium. The secondary complex generally crystallizes from the reaction medium in the form of bright crystals. The acidity of the chromating media must be such that the pH is nearly 2. It is also possible to produce the primary complex intermediately and to continue the chromating operation after acidification of the mixture.

The formation of the primary or secondary complexes can take place in an open vessel or under pressure in presence or in the absence of organic solvents, of mineral or organic salts; it can be applied as well to the pure dyestuffs as to their mixtures, eventually with other dyestuffs than those which are defined in the present specification. It is also possible to produce mixed complexes containing a plurality of metals through a treatment by means of mixtures of metal salts able to form complexes.

The chromiferous complexes of the category "III" can be used either for dyeing or for printing animal fibres. These dyestuffs have a remarkable affinity for chrome-leather which they permit to dye in united bright shades of good solidity.

A certain number of these complexes are in the state of free acids soluble in organic solvents and can be used for the coloration of varnishes, films, pellicles and the like.

Finally, remarks similar to those made for the dyestuffs of the category "II" can be made with respect to the greenish yellows.

It is, moreover, possible to obtain dyestuffs of the category "III" by sulphonation of the metalliferous complexes of the dyestuffs of the general formula "I".

The following are various examples for the application of the invention:

EXAMPLE 1

187 parts of 2-amino-3-naphtoic acid are diazotated by means of 250 parts of hydrochloric

acid of 19°Be, 2000 parts of water, 138 parts of sodium nitrite in solution of 50% and the quantity of ice which is necessary for maintaining the temperature at +5° C. The so obtained diazo compound is poured in half an hour into the copulation bath prepared in the following manner:

177 parts of anilide of the acetylacetic acid are dissolved in 2000 parts of water by means of 115 parts of caustic soda in solution of 35° Bé. 450 parts of crystallized sodium acetate are added and the whole is cooled to 0° C to the volume 4000.

The dyestuff, which gradually precipitates as its formation proceeds is separated in the usual manner. It appears in the form of a yellow powder which is almost insoluble in water, even in the state of sodium salt.

37,6 parts of the so obtained dyestuff are pasted in 250 parts of ethyl alcohol. A solution of chromium sulphate representing 7,8 parts of Cr²O³ in 25 parts of water and 5 parts of sulphuric acid of 36° Be is added.

The whole is then heated during 18 hours at 120° C in the autoclave. The so obtained product is treated with twice 500 parts of water in order to remove the chromium sulphate in excess.

The separated and dried dyestuff appears in the form of a yellow powder which is very soluble in organic solvents.

The applications of the solutions of this dyestuff in cellulosic varnishes give very bright greenish yellows or yellow greens which are solid to light and setting off.

EXAMPLE 2

To the diazo solution obtained according to example I a solution of 110 parts of resorcinol in 500 parts of cold water is added. Then the whole is poured during one hour into a solution of 180 parts of sodium carbonate. The so obtained dyestuff, which gradually precipitates as it is formed is separated in the usual manner.

30,8 parts of the so obtained dyestuff are pasted in 250 parts of ethyl alcohol. A solution of chromium sulphate representing 7,8 parts of Cr²O³ in 25 parts of water and 5 parts of sulphuric acid of 36° Be is added.

The whole is then heated during 12 hours at 120° C. in an autoclave. The crude formation is taken again with water and filtered. The so obtained precipitate is copiously washed in water in order to remove the chromium sulphate in excess.

The separated and dried dyestuff appears in the form of a brown powder which is soluble in organic solvents.

It tints the cellulosic varnishes in orange brown which is solid to light and setting off.

EXAMPLE 2 BIS

30,8 parts of the non-chromated dyestuff described in example 2 are treated with 400 parts of water at 90° and 12 parts of caustic soda of 35° Be. A solution of 14 parts of cobalt nitrate in 100 parts of water is added. The whole is maintained at 90° C. during half an hour and 15 parts of crystallizable acetic acid are added.

The so obtained dyestuff is soluble in organic solvents and in alcohol varnishes, which it permits to tint in brown yellow of good solidity.

EXAMPLE 3

The diazo solution obtained in the example 1

is poured into a solution obtained by dissolving 144 parts of bethanaphtol in 2000 parts of warm water and 115 parts of caustic soda in a solution of 35° Bé, by adding 180 parts of sodium carbonate and by cooling to 0° C.

The dyestuff, which precipitates as it is formed, is very little soluble in water.

When converted into a chromated complex in the same conditions as the dyestuff of example 1, it gives a brown black powder which is soluble in organic solvents.

The applications of the cellulosic varnishes tinted by means of this product are of a bordeaux-red colour.

EXAMPLE 4

267 parts of 2-amino-3-naphto-sulphonic acid obtained by sulphonation by means of the sulphuric monohydrate of the 2-amino-3-naphtic acid are dissolved in 2000 parts of cold water by means of 345 parts of caustic soda of 35° Bé. 138 parts of a solution of sodium nitrite of 50% are added and the whole is ice-cooled to 0°. 600 parts of hydrochloric acid of 19° Bé are poured as rapidly as possible into this solution. The so obtained diazo compound immediately precipitates in the form of light yellow crystals which are absolutely insoluble in water. The whole is filtered in order to remove the salt matters and re-pasted in 1000 parts of water at 0°.

On the other hand, a solution of 189 parts of paratoluidid of the acetylacetic acid in 2000 parts of water by means of 115 parts of caustic soda of 35° Bé. is prepared and 300 parts of crystallized sodium acetate are added. This solution is cooled at 0°.

A solution of copulating agent is rapidly poured into the pasting of the diazo derivative. The formation of the dyestuff is very rapid. It takes a gelatinous form; the mass is stirred during two hours at a low temperature and heated during one hour to 70° C. The formation is then saturated by means of diluted hydrochloric acid up to a weakly purple reaction with "Congo". The dyestuff crystallizes in a very good form.

When separated, dried and converted into a sodium salt it appears in the form of a yellow-green powder. It dyes wool in yellow-green which after running through bichromate bath turns excessively little into another colour.

The dyes of this dyestuff when run through a bichromate bath are solid to friction, to alkaline fulling and to light.

EXAMPLE 5

In the preparation of the preceding dyestuff the paratoluidid of the acetylacetic acid is substituted by 201 parts of metaxylidid of the acetylacetic acid.

The so obtained dyestuff, which is a little deeper than the preceding one but of the same shade possesses a very strong affinity for chrome-leather which it dyes in very green yellow which is very deep in colour and of good solidity.

EXAMPLE 6

A diazo solution identical to the solution of example 1 is prepared and poured during half an hour into the copulation bath obtained in the following manner:

254 parts of 1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid are dissolved in 2000 parts of

water and 115 parts of a solution of caustic soda of 35° Bé. 45 gr. of crystallized sodium acetate are added and the whole is then cooled to 0° C.

The copulation is very rapid.

The so obtained dyestuff dyes wool by the bichromate method in orange yellow. The obtained dyes are solid to fulling and to light.

The natural and artificial cellulosic fibres are perfectly well preserved.

EXAMPLE 7

A pasting of the diazo derivative used in example 4 is produced and a copulation bath obtained in the following manner is poured into this pasting:

174 parts of 1-phenyl-3-methyl-5-pyrazolone are dissolved in 2000 parts of water by means of 115 parts of a solution of caustic soda of 35° Bé. 450 parts of crystallized sodium acetate are added and the whole is ice-cooled to 0° C.

When the copulation is achieved a quantity of sulphuric acid of 36° Bé is added which is sufficient for causing the formation to become slightly acid with "Congo" red. The dyestuff which precipitates in an excellent form is thoroughly washed with a solution of sulphuric acid of 1% and can be considered as free from salt materials. When converted into a sodium salt through blending with carbonate, it dyes wool in orange yellow which is well united and solid to light and to alkaline fulling.

EXAMPLE 8

347 parts of 2-amino-3-naphto-disulphonic acid are dissolved in 4000 parts of boiling water. The solution is left to cool to the ordinary temperature and 150 parts of hydrochloric acid of 19° Bé are added. It is ice-cooled to 0° C. and 138 parts of a solution of sodium nitrite of 50% are poured during half an hour into this solution. The diazo derivative is entirely soluble in water. By a protracted stirring it crystallizes by and by.

The diazo compound is neutralized by the addition of crystallized sodium acetate up to a weak purple reaction with "Congo".

On the other hand a solution of copulating agent is prepared in the following manner: 207 parts of ortho-anisidid of the acetylacetic acid are dissolved in 2000 parts of water by means of 115 parts of caustic soda of 35° Bé. 300 parts of crystallized sodium acetate are still added and the whole is ice-cooled to 0° C.

The diazo compound is rapidly poured into this bath of copulating agent. The copulation is very rapid. The dyestuff precipitates partially. Sulphuric acid of 36° Bé is added up to a purple reaction with "Congo". The precipitation is complete.

When separated in the usual manner the dyestuff dyes animal fibres in yellow-green which after chromating has a good solidity to light and fulling.

EXAMPLE 9

In the production of the dyestuff of example 8 the ortho-anisidid of the acetylacetic acid is substituted by 174 parts of phenyl-methyl-pyrazolone. The so formed dyestuff is entirely dissolved. It is separated by acidification and salting out with sodium sulphate.

It dyes animal fibres in orange yellow which after chromating becomes solid to fulling and to light.

The natural and artificial cellulosic fibres are perfectly well preserved.

EXAMPLE 10

A diazo derivative identical to that of example 4 is produced. The pasting is poured during one hour into a copulation bath obtained in the following manner: 110 parts of resorcinol are dissolved in 500 parts of cold water and 180 parts of sodium carbonate. The whole is then ice-cooled to 0° C.

The dyestuff, which precipitates partially, is separated by acidification with sulphuric acid.

It dyes wool in orange brown which after chromating turns to brown red. The obtained dyes are solid to washing, fulling and light.

EXAMPLE 11

In the production of the dyestuff of Example 6 the solution of the copulating agent is substituted by a solution obtained in the following manner:

247 parts of 2-naphtol-6-sulphonate of sodium are dissolved in 2000 parts of water, 180 parts of sodium carbonate are added and the whole is ice-cooled to 0° C.

The so obtained dyestuff dyes wool in bright crimson. After running through a bichromate bath the dye becomes bordeaux and has a good solidity.

EXAMPLE 12

A diazo derivative identical with that of Example 4 is produced. The pasting is poured during one hour into a copulation bath obtained in the following manner:

144 parts of beta-naphtol are dissolved in 2000 parts of water by means of 115 parts of caustic soda and 180 parts of sodium carbonate. The whole is then ice-cooled to 0° C.

The dyestuff which forms is separated in the usual manner and converted into a sodium salt; it dyes wool in bright red which through chromating turns to bordeaux. The obtained dyes are solid to light and fulling.

EXAMPLE 13

In the production of the dyestuff of Example 12 the beta-naphtol is substituted by 108 parts of paracresol. The so obtained product when separated through acidification dyes wool in yellow brown which through chromating turns to purple brown.

The obtained dyes have a remarkable solidity to fulling.

EXAMPLE 14

A pasting of a diazo derivative identical with that of Example 4 is produced. A solution of copulating agent prepared in the following manner is rapidly poured: 108 parts of metaphenylen-diamine are dissolved in 2000 parts of water and 300 parts of crystallized sodium acetate are added.

The so obtained dyestuff dyes wool in bordeaux which through chromating turns to brown. The obtained dyes are solid to light.

EXAMPLE 15

A diazo derivative identical with that of Example 4 is produced. The pasting is poured in an hour into a copulation bath obtained in the

following manner: 224 parts of Néville-Winther acid are dissolved in 2000 parts of water by means of 115 parts of caustic soda of 35° Bé. 180 parts of sodium carbonate are still added and the whole is ice-cooled to 0°.

The so obtained dyestuff when separated through acidification and salting out with sodium sulphate dyes wool in bright red which through chromating gives a bright reddish purple which is solid to light and fulling.

The natural and artificial cellulosic fibres are perfectly well preserved.

EXAMPLE 16

A diazo derivative identical with that of Example 4 is produced and the pasting is rapidly poured into a copulation bath produced in the following manner: 143 parts of beta-naphtylamine are pasted during a few hours in 500 parts of water and 120 parts of hydrochloric acid of 19° Bé. 450 parts of crystallized sodium acetate are still added and the whole is ice-cooled to 0° C.

The dyestuff, which precipitates as it forms, dyes wool in crimson which after chromating turns to purple with good general solidities.

EXAMPLE 17

50 parts of the dyestuff of Example 3 are slowly introduced at the ordinary temperature into 500 parts of sulphuric monohydrate. The mixture is then heated during one hour to 50° C. and maintained at this temperature during one hour.

After this time the sulphonation is complete. The whole is left to cool to the ordinary temperature. It is then poured into 500 parts of ice. The dyestuff which first remains in solution precipitates and can be separated by filtration.

It appears in the form of a black powder which is soluble in water and sodium carbonate.

It dyes wool in red which turns to bordeaux through a treatment with bichromate.

EXAMPLE 18

A diazo derivative identical with that of Example 4 is produced and the pasting is poured into a copulation bath obtained in the following manner: 238 parts of 1-amino-8-oxynaphtalen-4-sulphonic acid are dissolved in 2000 parts of water by means of 115 parts of caustic soda. 120 parts of sodium carbonate are still added and the whole is ice-cooled to 0° C.

The dyestuff partially precipitates during its formation. It is separated by salting out with sodium sulphate.

It dyes wool in bright red which through chromating gives a grey blue of good solidity.

The natural and artificial cellulosic fibres are perfectly well preserved.

EXAMPLE 19

46,8 parts of the dyestuff produced in the Example 4 are pasted in 500 parts of water. A solution of chromium sulphate representing 7,8 parts of Cr²O³ in 25 parts of water and 10 parts of sulphuric acid of 36° Bé is then added.

The whole is then heated during 20 hours at 120-125° C. in the autoclave. The secondary chromated complex is entirely precipitated. After filtration it is converted into an alkaline salt by mixing with caustic soda in a sufficient quantity.

It dyes wool in an acid bath in yellow green solid to light and to fulling.

EXAMPLE 20

56.6 parts of the dyestuff produced in the Example 8 are dissolved in 1500 parts of boiling water. A solution of chromium sulphate representing 7.8 parts of Cr_2O_3 in 25 parts of water and 10 parts of sulphuric acid of 36° Bé is then added.

The whole is then heated with reflux during 12 hours. The dyestuff is first entirely converted into a primary chromated compound and then into a secondary complex which precipitates.

The obtained product appears in the form of a yellow green powder. It dyes wool in yellow green solid to light while perfectly preserving the natural and artificial cellulosic fibres.

EXAMPLE 21

45.3 parts of the dyestuff of example 7 are pasted in 500 parts of water. A solution of chromium sulphate representing 7.8 parts of Cr_2O_3 in 25 parts of water and 10 parts of sulphuric acid of 36° Bé. is then added. The whole is then heated at 115–120°C. during 12 hours in an autoclave.

After this time the secondary chromium dyestuff is entirely precipitated and there remains no trace of primary chromium compound.

It is to be noted that the dyestuff of example 7 is free from salt materials. The conversion into a secondary compound is complete. The conversion into an alkaline salt takes place as in example 18.

The obtained product dyes chrome-leather in bright orange, with a very high yield and of high brightness.

EXAMPLE 22

45.3 parts of the dyestuff of example 6 are dissolved in 1500 parts of boiling water. A solution of chromium sulphate representing 7.8 parts of Cr_2O_3 in 25 parts of water and 10 parts of sulphuric acid of 36° Bé. is then added. The whole is then heated with reflux during 20 hours.

After two hours heating the primary dyestuff is entirely formed and takes a very gelatinous form, then the secondary dyestuff forms.

The obtained product dyes wool in orange yellow solid to fulling and to light and of a good brightness.

The natural and artificial cellulosic fibres are perfectly well preserved.

The primary complex which has been formed intermediately can be separated by salting out. It dyes wool in an acid bath in yellowish orange which is less bright than the secondary dyestuff, but with a higher yield.

EXAMPLE 23

A solution of 50.2 parts of the dyestuff of example 14 in 1500 parts of water is heated during 10 hours with reflux with a solution of 15 parts of copper sulphate in 200 parts of water.

The copper compound, which has been precipitated by salting out, is separated. It dyes wool in bordeaux solid to light, preserving the natural and artificial cellulosic fibres in white.

EXAMPLE 24

10 parts of the dyestuff of example 1 are dissolved in 1000 parts of a cellulosic varnish on the

basis of nitro-cellulose. The dissolution is very rapid and the obtained solution is perfectly transparent. The applications of this varnish are of a deep yellow green colour solid to light and setting off.

EXAMPLE 25

2 parts of the dyestuff of example 4 are dissolved in 4000 parts of warm water and 5 parts of ammonium sulphate and 2 parts of acetic acid are added. 100 parts of wool are introduced at 50°C. The whole is manipulated during half an hour while heating to ebullition. 2 parts of sulphuric acid are still added and the ebullition is maintained further during half an hour.

The dyestuff dyes wool in very bright yellow green.

A bath of 1.5 parts of potassium bichromate and 2 parts of sulphuric acid in 1000 parts of water is prepared and heated at 60°C. The above mentioned dyed wool is introduced; it is heated up to ebullition and still manipulated during one hour at this temperature.

It is then copiously rinsed, dehydrated and dried.

The wool is then dyed in yellow green scarcely more red than the direct dye. The obtained dyes are solid to fulling and light.

EXAMPLE 26

100 parts of freshly neutralized chrome-leather are introduced into a fulling-mill containing 200 parts of water at 60° C. The fulling-mill is then set in motion. It is allowed to run a few minutes and through the hollow shaft of the mill $\frac{1}{2}$ of the solution obtained by dissolving 4 parts of the dyestuff of example 5 in 50 parts of water are added. The mill is then allowed to run during 15 minutes; the remainder of the dyestuff is added and the mill is allowed to run 25 to 30 minutes. The leather is put on the frame and the dye is achieved according to the usual technics.

The leather is dyed in very bright deep yellow green of good solidity.

EXAMPLE 27

2 parts of the dyestuff of example 22 are dissolved in 4000 parts of warm water; 5 parts of ammonium sulphate and 2 parts of sulphuric acid of 36° Bé. are added. 100 parts of wool are introduced at 50° C. It is heated to ebullition during half an hour and still manipulated at this temperature during one hour. The dye bath is very well exhausted. The wool is taken out, thoroughly rinsed, dehydrated and dried.

The wool is dyed in bright reddish purple of good solidity.

EXAMPLE 28

1 part of the dyestuff of example 11 is dissolved in 100 parts of water. 50 parts of barium sulphate and 10 parts of aluminum sulphate are added; the whole is heated to 50° C and a solution of 10 parts of crystallized barium chloride in 20 parts of warm water is poured into the mass. The latter is then heated to ebullition, filtered and washed. The so prepared bordeaux lacquer is solid to light and can be used for paints, graphic inks, colours for whitewashing and for wall papers.

The following table gives a summary of the properties of some dyestuffs produced according to the invention:

	Constitutions	Shade in varnishes	Shade on chrome-leather	Shade on wool	Shade on wool after chromating	Applications
1	2. amino-3-naphtoic acid → acetoacetanilide (chromated).	Yellow green				Coloration of solvents, varnishes, plastic materials, rayon silks in the mass.
2	2. amino-3-naphtoic acid → acetoacetyl-m-xylidine (chromated).	do.				Do.
3	2. amino-3-naphtoic acid → phenyl-methyl-pyrazolone (chromated).	Orange yellow				Do.
4	2. amino-3-naphtoic acid → resorcinol (chromated).	Brown red				Do.
5	2. amino-3-naphtoic acid → betanaphthol (chromated).	Bordeaux				Do.
6	2. amino-3-naphto-sulphonic acid → acetoacetanilide.		Yellow green	Yellow green	Yellow green	Coloration of chrome-leather wool, pure or loaded lacquers.
7	2. amino-3-naphto-sulphonic acid → acetoacetyl-p-toluidine.		do.	do.	do.	Do.
8	Secondary chromated derivative of "7".		do.	do.		Do.
9	2. amino-3-naphto-sulphonic acid → acetoacetyl-p-cresidine.		do.	do.	Yellow green	Do.
10	2. amino-3-naphto-sulphonic acid → acetoacetyl-amino-hydroquinone-diethylether.		Clear yellow	Clear yellow	Clear yellow	Do.
11	2. amino-3-naphto-disulphonic acid → acetoacetanilide.		Yellow green	Yellow green	Yellow green	Do.
12	Secondary chromated derivative of "11".		do.	do.		Do.
13	2. amino-3-naphto-disulphonic acid → acetoacetyl-o-anisidine.		do.	do.	Yellow green	Do.
14	Secondary chromated compound of "13".		do.	do.		Do.
15	2. amino-3-naphto-disulphonic acid → acetoacetyl-m-xylidine.		do.	do.	Yellow green	Do.
16	2. amino-3-naphtoic acid → sulpho-phenyl-methyl-pyrazolone.		Orange yellow	Clear yellow	Orange yellow	Do.
17	Secondary chromated compound of "16".		do.	Orange yellow		Do.
18	2. amino-3-naphto-sulphonic acid → phenyl-methyl-pyrazolone.		do.	Clear yellow	Orange yellow	Do.
19	Secondary chromated compound of "18".	Orange yellow	do.	Orange yellow		Coloration of varnishes, dyeing of chrome-leather, wool.
20	2. amino-3-naphto-sulphonic acid → 2'-chlorophenyl-methyl-pyrazolone-5'-sulphonic acid.		do.	Clear yellow	Orange yellow	Dyeing of wool and chrome leather.
21	Secondary chromated compound of "20".		do.	Orange yellow		Do.
22	2. amino-3-naphto-sulphonic acid → phenyl-methyl-pyrazolone.		do.	Clear yellow	Orange yellow	Do.
23	1. amino-3-naphto-sulphonic acid → resorcinol.		Brown red	Crimson	Brown red	Do.
24	Secondary chromated compound of "23".	Orange brown	do.	Brown red		Coloration of varnishes, dyeing of wool and chrome-leather.
25	2. amino-3-naphto-disulphonic acid → resorcinol.		do.	Crimson	Brown red	Dyeing of wool and chrome-leather, preparation of lacquers.
26	2. amino-3-naphto-sulphonic acid → p.cresol.		Purplish brown	Yellow brown	Purplish brown	Do.
27	2. amino-3-naphto-disulphonic acid → p.cresol.		do.	do.	do.	Do.
28	2. amino-3-naphtoic acid → metaphenylen-diamine-sulphonic acid.		Brown	Red brown	Brown	Do.
29	2. amino-3-naphto-sulphonic acid → metaphenylen-diamine.		do.	do.	do.	Do.
30	2. amino-3-naphto-sulphonic acid → metaphenylen-diamine-sulphonic acid.		do.	Bordeaux	do.	Do.
31	2. amino-3-naphto-disulphonic acid → metaphenylen-diamine.		do.	Red brown	do.	Do.
32	2. amino-3-naphtoic acid → 2-naphthol-6-sulphonate of sodium.		Bluish red	Crimson	Bordeaux	Do.
33	2. amino-3-naphto-sulphonic acid → beta-naphthol.		do.	do.	do.	Do.
34	2. amino-3-naphto-disulphonic acid → beta-naphthol.		do.	do.	do.	Do.
35	2. amino-3-naphto-sulphonic acid → Neville-Winter acid.		Purple	Red	Purple	Do.
36	Secondary chromated compound of "35".		do.	Purple		Do.
37	2. amino-3-naphto-sulphonic acid → 8-acid.		Purplish blue	Bordeaux	Grey blue	Do.

GEORGES KOPP.
RENÉ EUGÈNE MARCEL GANGNEUX.