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PROCESS FOR THE PREPARATION IN AN
ACID MEDIUM OF CHROMED DYESTUFFS
AND PRODUCTS RESULTING FROM THIS
PROCESS

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In U. S. Patent No. 1,921,586 is described a process for the preparation of chromed complexes of ortho-hydroxy-azo dyestuffs consisting in treating these dyestuffs with salts of chromium with a mineral acid radicle without effecting the neutralization customarily recommended of the mineral acid liberated in the course of the fixation of the chromium on the coloring material. It has been indicated in addition that this treatment can be effected in the presence of a free mineral acid added to the bodies taking part in the reaction and more particularly in the presence of sulphuric acid. This process permits of obtaining chromed dyestuffs of which the shade and the properties are considerably different from those of the chromed dyestuffs obtained by the customary methods in the absence of mineral acid. Actually it has been found that the formation of these new chromed compounds takes place in two principal phases.

In the first place the ortho-hydroxy-azo dyestuffs form, with the oxide of chromium yielded by the chromium salts, chromed compounds which are very soluble in water, characterized by an excellent affinity for the animal fibre but in general having the disadvantage of being too sensitive to the action of acids. The dyeings obtained by means of these products are generally strong, of flat shades and often uneven. These products which are obtained most easily in a neutral or very slightly acid medium are precisely those to which are directed the processes in which a neutralization is effected of the liberated acid. They will be designated in the present application by the expression "primary chromed compounds".

In the second place under the prolonged action of the chroming media rendered strongly acid by the presence of the mineral acid derived from the chromium salts and if desired by the previous addition of acid, these primary compounds are converted into other chromed compounds characterized chiefly by their great resistance to acid agents of all types. Compared with the primary products which correspond thereto the new dyestuffs present the advantage of giving brighter and more even shades. In addition they are generally more resistant to the action of light. They contain in general the same number of atoms of chromium per molecule. These compounds will be designated in the present application by the expression "secondary chromed compounds".

An analogous conversion of primary chromed compounds into secondary chromed compounds is obtained by the process which was the object

of U. S. Patent No. 1,924,696 and which consists in heating in the presence of dilute sulphuric acid the chromed complexes of certain ortho-hydroxy-azo dyestuffs. By this process the transformation is carried out, as by the process of the Patent No. 1,921,586, in a mineral acid medium, but the phase of transformation is quite distinct from the phase of formation of the primary chromed compounds, the latter being previously obtained by any known processes. In addition the Patent No. 1,924,696 only contemplates the application of the process to a relatively limited class of chromed complexes of ortho-hydroxy-azo dyestuffs, those derived from the dyestuffs obtained by the coupling of ortho-aminophenols or ortho-aminonaphthols and their substitution products with pyrazolones.

Now it has been found in accordance with the present invention that in a general manner it is possible to cause the conversion of primary chromed compounds into secondary chromed compounds by subjecting the former to a treatment in an acid medium, the acidity being obtained either by the addition of any suitable mineral, organic or sulpho-aromatic acids or by salts of acid character or compounds capable of providing acid compounds or also by mixtures comprising several of these products and that in addition this treatment is applicable to all the ortho-hydroxy-azo dyestuffs.

The conversion process can likewise be effected in a very varied manner. In particular the conversion can be effected in the presence of products taking no part in the specific reaction of the acids.

It is for example possible to apply the process of the invention without separating the ortho-hydroxy-azo dyestuffs from their coupling media or media from the first phase of chroming. It is also possible to apply the conversion treatment in an acid medium to primary chromed compounds obtained by the customary processes and isolated from their media of formation.

This treatment can be effected under all conditions of temperature, volume or pressure and if desired in the presence of organic solvents. However it has been found that the conversion takes place particularly well in the absence of electrolytes, that is, materials capable of evolving acid ions and basic ions under the action of an electric current; this absence permits chiefly the lowering of the temperatures of the reactions and the shortening of their duration.

In certain cases the general process according to the invention permits of effecting an economy

of chromium. For example the primary chromed compound obtained by the action of the chromium sulphate in the presence of sodium acetate on the azo dyestuff mentioned in Patent No. 1,924,696 and containing $\frac{1}{2}$ molecule of $\text{Cr}(\text{OH})_3$ per molecule of dyestuff, is converted in accordance with Example 7 of the present application into a new chromed compound which is a well defined crystalline substance dyeing wool a bright rose color.

This compound likewise contains $\frac{1}{2}$ molecule of $\text{Cr}(\text{OH})_3$ per molecule of dyestuff. However, it exhibits the same very advantageous tinctorial properties as the dyestuff obtained by heating under pressure for 24 hours of the same starting azo dyestuff in the presence of a solution of chromium sulphate according to Example 1 of Patent No. 1,921,586 and which contains 1 molecule of $\text{Cr}(\text{OH})_3$ per molecule of dyestuff.

It has further been found that the process of the invention can be applied advantageously to the mixture of dyestuffs containing metals, thus giving rise to the formation of new homogeneous products which it would be impossible to prepare by mixing chromed compounds obtained separately (for example according to the process of either one of the patents above referred to) the inferiority of such mixtures being shown particularly when the constituents exhibit in addition to differences of shades very different physical or chemical properties. If for example a very soluble dyestuff is mixed with a difficultly soluble dyestuff it is difficult to obtain level shades; it is the same when the constituents of the mixture have for the textile fibres unequal affinities. These disadvantages are eliminated for the products obtained in accordance with the new process, the individual properties of the constituents having disappeared.

The new process can likewise be applied in such a manner as to obtain not only the pure secondary compounds but also mixtures of primary or secondary compounds.

The following examples illustrate the present invention without limiting the same thereto.

Example 1

There are heated under reflux for several hours 30 parts of the azo dyestuff obtained by the coupling of the diazo derivative of 1-hydroxybenzene-2-amino-4-sulphonic acid and 1-phenyl-3-methyl-5-pyrazolone with 25 parts of chrome alum, 15 parts of crystallized sodium acetate and 600 parts of water. After several hours heating the whole has passed into solution. The chromed compound thus formed dyes wool from an acid bath in orange red shades. It exhibits the disadvantage of being very uneven and of being converted by dilute acids into an orange yellow product.

On continuing the heating the crystallization is found to take place of a dyestuff which is very difficultly soluble in water. After 24 hours heating the whole is precipitated and the primary reddish compound is found to have completely disappeared. The secondary compound dyes wool in orange yellow shades which are more even and more resistant to light than the primary compound.

The dyestuff thus obtained is identical with that which is formed when the primary compound isolated by salting out is treated with an acid compound for example under the conditions of Patent No. 1,924,696.

The secondary compound is obtained as free acid practically insoluble in water and in most

organic solvents. It can be employed in the form of pigments fast to light.

Converted into soluble salt, for example into the sodium salt, it can be employed for the dyeing of natural or artificial textile fibres in an alkaline, neutral, or acid bath. Its solubility in organic solvents permits of its use in the coloring of varnishes and plastic masses.

Example 2

There are heated in an autoclave 30 parts of the azo dyestuff obtained by coupling the diazo-compound of 1-amino-naphthalene-2-hydroxy-4-sulphonic acid and β -naphthol with 10 parts of common salt, 10 parts of chromium formate containing 40% of Cr_2O_3 , 15 parts of crystallized sodium acetate and 500 parts of water. After 2 hours heating at 105°C . the whole has passed into solution and non-chromed dyestuff can no longer be detected.

The product obtained dyes wool in a neutral or acid bath a dull grey blue. This product is decomposed under the action of acids on the one hand into non-chromed dyestuff and on the other hand into a new chromed compound difficultly soluble in water.

In order to obtain only the secondary chromed compound there are added to the primary compound obtained in accordance with the first paragraph of this example 10 parts of hydrochloric acid of 30% HCl and the heating is continued for 6 hours to 105°C . It is then found that the new chromed compound has been almost completely precipitated. It is soluble in alkalies with the formation of salts which can be isolated by salting out and filtration. The products thus obtained dye animal fibres in a neutral or acid bath in a pure fast blue.

The secondary compound is distinguished from the primary compound likewise by the following reactions.

The aqueous solutions of the sodium salts exhibit very different changes of color in contact with the following chemical agents:

	$\text{HCl } 10\% \text{ B\acute{e.}}$	$\text{NaOH } 5\%$	$\text{Na}_2\text{CO}_3 \text{ } 10\%$
Primary compound	Grey.....	Black red...	Blue black
Secondary compound.	Bright blue green.	Bright violet.	Violet red.

The colorations of the solutions in pure concentrated sulphuric acid are as follows:

Primary compound: bright indigo blue.
Secondary compound: flat blue green.

Example 3

30 parts of the azodyestuff obtained by the coupling of the nitro-diazo derivative of 1-amino-naphthalene-2-oxy-4-sulphonic acid and β -naphthol are heated to 120°C . with 500 parts of water, 50 parts of a solution of chromium naphthalene-1.5-disulphonate containing 5% of Cr_2O_3 and the quantity of caustic soda necessary in order to neutralize the mineral acid of the mixture thus obtained.

After 6 hours heating the whole has passed into solution.

If the dyestuff is precipitated at this point it is constituted by practically pure primary chromed compound. It dyes wool from an acid bath a very full reddish black, sensitive to the action of acids of all types which cause the

original reddish black shade to change to greenish black.

Instead of isolating the primary chromed compound 10 parts of formic acid can be added and heating continued for a further two hours at 100° C. Then the formation of the secondary chromed compound is found to take place which separates in the crystalline form. Salt is added to complete the precipitation and the product is filtered and dried.

The dyestuff obtained is very different from that obtained in the first place. It constitutes a mixture of the primary and secondary chromed compounds; the formation of the latter is due to the action of the formic acid.

If the heating in the presence of formic acid is prolonged the secondary compound is obtained in the pure state.

The secondary compound is converted into soluble salt. It dyes wool greenish black very even shades.

The mixtures of the primary and secondary compounds give blacks which are very interesting on account of their shades and their fastness properties. They likewise permit dyeing in pure fast grey shades.

When the mixtures are rich in secondary compound it is of advantage to render them soluble by salt formation.

Example 4

To the products employed in the example of Patent No. 1,924,696 (that is to say the red blue chromed complex obtained in the absence of mineral acid starting from 42.5 kg. of the azo dyestuff prepared by the action of the diazo compound of 1-amino-2-oxynaphthalene-4-sulphonic acid on 1-phenyl-3-methyl-5-pyrazolone and to which are added 400 litres of water with the addition of 8 kgs. of sulphuric acid of 66° Bé.), are added 5 kgs. of the primary chromed compound of the azo dyestuff obtained by coupling the diazo derivative of 1-aminobenzene-2-oxy-4-sulphonic acid with β -naphthol. Then the whole is heated in a lead-lined autoclave under pressure to 120° C. for 20 hours according to the directions of Patent No. 1,924,696.

A bluish red is obtained which is very soluble and in which it is not possible to detect the two components. The dyestuff dyes animal fibre a Bordeaux shade which is very even.

The two compounds prepared separately and subsequently mixed do not permit of obtaining the same effect; the evenness is defective.

Example 5

20 parts of the primary dyestuff of Example 1 above are intimately mixed with 100 parts of water and 1 part of 96% sulphuric acid; the paste obtained is dried in a vacuum at 100° C. By this treatment a partial transformation is effected of the primary chromed compound into the secondary chromed compound. After solubilization, for example by conversion into the sodium salt, the dyestuff obtained dyes animal fibre in a neutral or acid bath a pure orange of very good fastness.

Example 6

20 parts of the pure primary chromed compound obtained by salting out and filtration of the first reaction product of Example 3 above are heated during 4 hours to 105° C. with 300 parts of water and 5 parts of hydrochloric acid containing 30% HCl. A dyestuff is obtained which is insoluble in the state of free acid but which after conversion into the ammonium salt can be employed for the dyeing of animal fibres in fast grey shades. This product exhibits physical, chemical and tinctorial properties which are very different from those of the primary product but it has the same molecular concentration of chromium oxide.

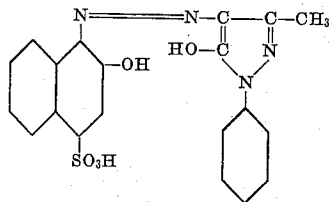
Example 7

25 parts are prepared of the primary chromed compound of the azo dyestuff resulting from the combination of 1-diazo-2-naphthol-4-sulphonic acid with 1-phenyl-3-methyl-5-pyrazolone; the primary chromed compound is obtained in accordance with the customary process for example by means of chromium sulphate and sodium acetate. This chromed dyestuff which is very soluble in water dyes wool a dull bluish red shade; it has the disadvantage of being uneven and of giving irregular shades on account of its sensitivity to the acids of the dye baths.

This compound is converted into the secondary compound by heating in an autoclave for 5 hours to 140° C. with 400 parts of water and 11 parts of benzene-sulphonic acid. The new chromed compound crystallizes in the form of bronze prisms practically insoluble in water. It exhibits the tinctorial properties of the dyestuff obtained according to Example 1 of Patent No. 1,921,586. However it only contains $\frac{1}{2}$ molecule of $\text{Cr}(\text{OH})_3$ while the dyestuff of Patent No. 1,921,586 contains 1 molecule per molecule of dyestuff.

I claim:

1. Process for the manufacture of a chromiferous azo dyestuff which dyes pink tints, consisting in heating with benzene sulfonic acid the chromium compound that dyes blue-red tints and is obtainable by the usual chroming methods from the azo dyestuff of the formula



2. Process for the preparation of chromed dyestuffs consisting in heating in an acid medium mixtures of azo dyestuffs each containing a metal, said dyestuffs being ortho-hydroxy-azo dyestuffs.

3. Chromed dyestuffs obtained by heating in an acid medium mixtures of azo dyestuffs each containing a metal, said dyestuffs being ortho-hydroxy-azo dyestuffs.

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