

# ALIEN PROPERTY CUSTODIAN

## NOVEL CHROMIFEROUS DYESTUFFS AND PROCESSES FOR MAKING THE SAME

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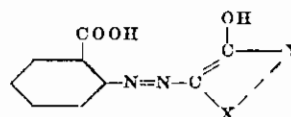
In the U. S. A. Patent N° 2,133,864 the existence of two kinds of chromiferous ortho-oxyazoic complexes has been pointed out, the ones of which are preferably formed in a neutral medium and will be called hereafter "primary chromium compounds," while the others are formed in an acid medium and will be called hereafter "secondary chromium compounds." In the above mentioned patent are described processes which permit to obtain, at will and in each case, the so-called "primary" and "secondary" complexes. The dyestuffs which are mentioned in this patent are exclusively ortho-oxy-azoic dyestuffs derived principally from orthoamidophenols and orthoaminophenols.

Now it has been found, according to the present invention, that the orthocarboxyazoic dyestuffs derived from orthoaminocarboxylic acids also lead to two kinds of chromiferous compounds, the ones of which are preferably formed in a neutral medium, while the others are exclusively formed in a strongly acid medium. However it will be noted that whilst most of the ortho-oxyazoic dyestuffs already form secondary complexes in a weakly acid medium, in the case of the orthocarboxyazoic dyestuffs the secondary complexes are more particularly formed in a strongly acid medium. The differences in the properties of the primary and secondary complexes are generally very marked. In all the cases the secondary complexes are brighter and unite remarkably well on wool in an acid bath, while the primary complexes unite so badly that their commercial use is in most cases excluded. Another advantage of the secondary complexes is the possibility of rapidly dyeing them in a weakly acid bath, while the primary complexes require high quantities of acid and very long durations of the dyeing operation.

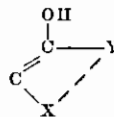
Although some chromium complexes of o-carboxyazoic dyestuffs have already been obtained in an acid medium the possibility of producing two kinds of ortho-carboxy-azoic chromium complexes was not hitherto known. It is said, for instance, in the French Patent N° 758,263 of July 12, 1933, in Example 2: Dyestuffs having similar properties are obtained when the chromidization is effected with other chromium salts." But the process of this example leads to the pure primary complex without any trace of secondary complex; the latter which, moreover, forms only in a chroming medium which is clearly acid to Congo red, dyes the animal fibres in a weakly acid bath in perfectly uniform golden yellow, while the pri-

mary complex used in the same conditions gives a very unequal yellow-orange tint.

More particularly it has been ascertained according to the present invention, that novel complexes of a high commercial interest are obtained by subjecting to the action of agents which are acid to Congo red, at a high temperature, the chromium complexes of the dyestuffs of the general formula



in which



represents the rest of a sulphonated arylpyrazolone, of a sulphonated naphthol or of a sulphonated arylide of acylacetic acid.

The dyestuffs which can be used as starting materials for carrying out the invention can be obtained by diazotation of the anthranilic acid and copulation of the obtained diazoic derivative with a sulphonated arylpyrazolone, a sulphonated naphthol or a sulphonated arylide of acylacetic acid; the above mentioned copulating agents may contain a plurality of SO<sub>2</sub>H groups and other substituents such as halogen atoms, the alkyl, alkoxy, carboxy, sulphamido groups and the like; they can also be obtained by sulphonation of non-sulphonated monoazoic compounds.

The secondary chromium compounds according to the invention can be obtained in one or more steps.

It is more particularly possible to first produce the primary compound in the absence of strong mineral acid and to convert this compound into a secondary complex. This conversion can be effected in the medium in which the production of the primary one has been effected or in another medium after isolation of the primary compound; it is sufficient to heat the chromium complex in the presence of any acid product such as sulphuric, hydrochloric, arylsulphonic acid or the like, in a sufficient quantity in order that the reaction mixture gives a clearly blue coloration with Congo red.

It is also possible to heat the orthocarboxyazoic dyestuff with a chromium salt in such conditions that the reaction is strongly acid at least at the end of the chroming treatment. This work-

ing method can be performed through the addition of any acid product in a sufficient quantity in order that the reaction mixture gives a clearly blue coloration with Congo red; it can also be performed by using as a chroming agent a chromium salt such as chromium sulphate and the arylsulphonates of chromium which give a sufficient acidity during the chroming treatment.

In certain cases even very small quantities of water soluble saline materials can retard the formation of the secondary complexes; in order to avoid this draw-back the starting dyestuffs are completely freed from saline materials by converting the said dyestuffs by any means into free acids; the obtained products are then subjected to the action of chroming agents in a medium which is acid to Congo red, as above mentioned.

The production of sulphonated azoic dyestuffs which are free from salts and in the state of free acids can be effected, in some cases, by treating alkaline salts with strong excesses of mineral acids. This process gives satisfactory results when the free acids are little soluble in the presence of an excess of mineral acid, but it can be used only if the reaction of the mineral acid with the dyestuff can be performed in such conditions that the mineral acid effectively displaces the free acid of the dyestuff. Another more general process consists in precipitating the dyestuffs in the form of earth-alkaline salts and in treating the so formed salts by sulphuric acid; thus an insoluble earth-alkaline sulphate and a dyestuff in the state of free acid are formed. The chromating operation can be effected either in the presence of the insoluble sulphate or after elimination of the latter, for instance in the cases in which the free acids of the dyestuffs are soluble in water.

The process according to the invention applies as well to the pure dyestuffs as to their mixtures eventually with dyestuffs which do not correspond to the above given definition.

The formation of the secondary complexes takes place in various conditions of temperature, volume and pressure.

The secondary orthocarboxyazoic chromiferous complexes according to the invention can be used for the coloration of fibres of all kinds such as wools, artificial protein fibres, leathers, hides and the like. Certain of these chromiferous complexes are soluble in organic solvents and can be used in the manufacture of varnishes, plastic materials, fatty bodies and the like.

The following examples of execution of the invention are given by way of non-limiting examples.

#### Example 1

40.4 parts of the monosodic salt of the azoic dyestuff obtained by copulation of the 2-diazo-benzene-1-carboxylic acid with the 1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid are dissolved in 500 parts of water, and 20 parts of chromium formiate are added and the whole is heated on reflux during several hours. The primary chromiferous complex obtained which is very soluble, is isolated by salting out. It dyes the wool in an acid bath in rather dull reddish yellow with the disadvantage of uniting very badly.

When subjected in the boiling state to the action of diluted mineral acids this product gives a novel chromium compound, i. e. a secondary compound which is little soluble in water.

This secondary complex can be directly produced by heating on reflux during several hours 40.4 parts of the azoic dyestuff described in the

first paragraph of this example with 500 parts of water, 7.8 parts of  $\text{Cr}_2\text{O}_3$  in the form of a solution of chromium sulphate and 11.5 parts of sulphuric acid of 36° Bé. The chromiferous complex, which is little soluble, precipitates as it is formed in the form of splendid crystals. It is separated by filtration. When converted into a sodium salt it dyes the wool in an acid bath in a bright yellow tint which is very well united and possesses excellent properties of solidity.

#### Example 2

37.3 parts of the monosodic salt of the dyestuff obtained by copulation of the 2-diazo-benzene-1-carboxylic acid with the naphtol-sulphonic-1.5 acid, are dissolved in 500 parts of water and 11.5 parts of sulphuric acid of 36° Bé and 7.8 parts of  $\text{Cr}_2\text{O}_3$  in the form of a solution of chromium sulphate are added. After having heated on reflux during several hours, the secondary compound begins to precipitate in the form of bright crystals; heating is still continued during 6 to 8 hours and the dyestuff is separated by filtration. When converted into a sodium salt it dyes the wool in an acid bath in a bright violet tint which unites very well and has excellent properties of solidity. The primary compound which can be readily obtained by performing the chroming operation in a neutral medium with formiate or acetate of chromium, for instance, possesses dyeing properties of much less interest; it dyes the wool in an acid bath in a brownish violet tint which is dull and unites very badly.

The secondary compound also differs from the primary compound by the following reactions:

The aqueous solutions of the sodium salts show different changes in the contact of the following chemical agents:

	HCl 10°	NaOH 5%
Primary .....	Violet grey....	Orange grey.
Secondary compound .....	Bordeaux....	Orange.

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

Primary compound..... Brown  
Secondary compound..... Bottle green

#### Example 3

35 parts of the monosodic salt of the dyestuff resulting from the copulation of the 2-diazo-benzene-1-carboxylic acid with the 1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid are heated on reflux with 200 parts of water, 15 parts of chromium fluoride, 8 parts of pyridine and 15 parts of sulphuric acid of 36° Bé. After a few hours the formation of bright crystals is observed which are constituted of the secondary chromium complex which after being filtered and transformed into an alkaline salt dyes the wool in an acid bath in a perfectly united golden yellow.

The same reaction when made in the absence of sulphuric acid very rapidly leads to the primary complex which dyes the wool in a reddish yellow of very bad unison and which, therefore, is of no practical interest.

#### Example 4

10 parts of the monosodic salt of the dyestuff resulting from the copulation of the 2-diazobenzene-1-carboxylic acid with the 1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid are treated with 1000 parts of boiling water and a quantity of hydrochloric acid which is sufficient for

acidifying; then is added a solution of 15 parts of crystallized barium chloride in 100 parts of water. The barium salt of the dyestuff crystallizes and is isolated by filtration and then converted into free acid by a treatment with diluted sulphuric acid and elimination of the barium sulphate. 100 parts of a solution of basic chromium sulphate containing 15% of  $\text{Cr}(\text{OH})_3$  are added to the solution of free acid, the whole is heated on reflux until total conversion into a secondary chromium complex which crystallizes in the form of large scales having a metallic glow, then it is filtered and converted into a soluble alkaline salt. The novel dyestuff dyes animal and artificial fibres containing protein substances in a golden yellow having excellent properties of solidity.

#### Example 5

37.3 parts of the dyestuff resulting from the copulation of the diazotated anthranilic acid with the 1-napthol-5-sulphonic acid are dissolved in 500 parts of water; 10 parts of hydrochloric acid and 15 parts of crystallized barium chloride are then added. The barium salt obtained is isolated and converted into a free acid by means of sulphuric acid. 10.3 parts of chromium hydroxide and 15 parts of sulphuric acid of 36° Be are added to this product and the whole is heated on reflux until complete crystallization, filtered and converted into a sodium salt. The novel dyestuff dyes the animal fibres in an acid bath in violet colour.

#### Example 6

40.4 parts of the monosodic salt of the dyestuff resulting from the copulation of the diazotated anthranilic acid with the 1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid are dissolved into 1600 parts of water and 10 parts of pyridin. 15 parts of chromium fluoride are then added and the whole is heated on reflux. After having been heated during a few hours the dyestuff is completely converted into a chromium complex of the primary type. A continuation of the heating operation does no longer change the properties of this complex which can be isolated by salting or by evaporation in a dry state. This dyestuff,

which is very soluble in water, dyes the wool in an acid bath in reddish yellow of very bad unison. It can be converted into a complex of the secondary type in the following manner:

The dyestuff resulting from the application of the above described process is dissolved in 800 parts of water and 15 parts of sulphuric acid of 36° Be are added; then it is heated on reflux during several hours. The formation of crystals is observed which show a bronzed glow and are isolated by filtration. They are formed of secondary chromium complex in the state of a free acid. When converted into a soluble alkaline salt, the novel chromiferous complex dyes the wool in an acid bath in a perfectly uniform clear yellow.

#### Example 7

The process of example 5 is applied to the dyestuff obtained by copulation of the diazotated anthranilic acid with the naphthol-2-sulphonic-6 acid. The obtained secondary compound gives aqueous solutions of a bright yellowish red colour and dyes the animal fibres in an acid bath in unalterable red.

This novel process permits to obtain a rather complete range of valuable chromiferous dyestuffs. The anthranilic acid gives by diazotation, copulation and chroming in a strongly acid medium dyestuffs the colours of which vary according to the copulating agents. The shades which are obtained with various copulating agents are as follows:

Copulating agents	Tint of the dyeing on wool in an acid bath
Sulphonated acylacetic arylides and their substitution products.	Greenish yellows.
Sulphonated pyrazolones and their substitution products.	Clear yellows.
Beta-naphol-sulphonic acids in which position 1 is free.	Clear reds.
Alpha-naphol-sulphonic acids copulating in position 2.	Bordeaux and violets.

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