

UNITED STATES PATENT OFFICE

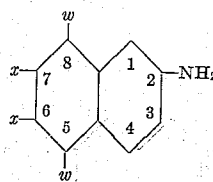
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METAL COMPOUNDS OF AZO-DYESTUFFS AND PROCESS OF MAKING SAME

No Drawing. Application filed March 8, 1929, Serial No. 345,588, and in Switzerland March 10, 1928.

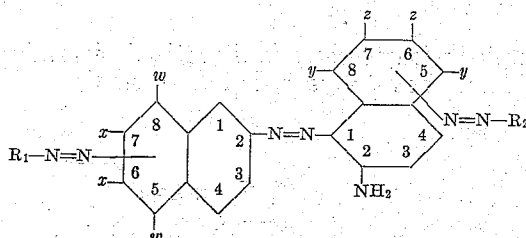
The present invention relates to new and valuable metal compounds of azo-dyestuffs deriving from metals of atomic weights ranging from 52 to 58.7. These metal compounds may contain either one metal alone or several metals. In the latter case one or several metals may also not belong to the above mentioned range of atomic weights. The dyestuffs according to the present invention are made by treating the poly-azo-dye-

stuff which is obtained by coupling a diazotized amino-naphthol of the general formula



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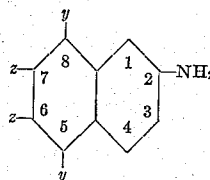
in which the one w represents one OH-group and the other w a hydrogen atom, the one x a SO_3H -group and the other x a hydrogen atom, and in which the sulfo-group stands in meta-position to the OH-group, in weak acid medium with an amino-naphthol of the general formula



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in which R_1 and R_2 are aryl residues, from which at least the one of these contains a mordant binding group in ortho-position to the $-\text{N}=\text{N}-$ group, and in which one of the w 's and one of the y 's stand for an OH-group and the other w and the other y for a hydrogen atom, one of the x 's and one of the z 's represent a SO_3H -group and the other x and the other z a hydrogen atom, the sulfo-groups being in meta-position to the OH-groups, further in which the two azo-groups are linked in ortho-position to the OH-groups and in which at most one OH-group stands in 8-position, with agents yielding metals of atomic weights ranging from 52 to 58.7, these agents being chosen in such a way that either one or several metals enter the dyestuff molecule whereby in the latter case other metals may also enter the dyestuff molecule. The treatment may be applied in the course of the production of the said poly-azo-dyestuff or to the finished dyestuff, either in the fiber, in the dye-bath or in substance. The dyestuffs of the above formula may be made, for example, by coupling two molecular proportions of diazo-compounds, at least the one component of which contains a mordant binding group in ortho-position to the $-\text{N}=\text{N}-$ group, with a mono-azo-dyestuff



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in which the two y 's and the two z 's have the same meaning as above indicated, these two amino-naphthols being chosen in such a manner that the resulting azo-dyestuffs contain at most in one 8-position one OH-group.

The metal compounds of the azo-dyestuffs of the above explained general formula deriving from metals of atomic weights ranging from 52 to 58.7 and which may contain still other metals are when dry dark colored powders soluble in water and dilute alkalies to blue to grey-blue and grey solutions and in concentrated sulfuric acid to blackish-blue to blue and grey solutions, and dyeing vegetable fiber and especially artificial silk from so-called regenerated cellulose fast violet to blue and grey tints. Particularly useful are those combinations which derive from the mono-azo-dyestuff produced by coupling one molecular proportion of diazotized 2-amino-5-hydroxynaphthalene-7-sulfonic acid with a second molecular proportion of the same aminonaphthol-sulfonic acid in a feebly acid medium. These dyestuffs, however, do not dye the artificial silks from cellulose esters or cellulose ethers.

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per and then with those yielding chromium, a dark powder is obtained which dissolves in water and dilute alkalis to blue-grey solutions and dyes cotton in an alkaline bath containing Glauber's salt blue-grey level tints.

The corresponding chromium compound of the dyestuff prepared from two molecules of diazotized 4-nitro-2-amino-1-phenol and 2:1'-azonaphthalene-5:5'-dihydroxy-2'-amino-7:7'-disulfonic acid dyes viscose green-grey tints.

Example 3

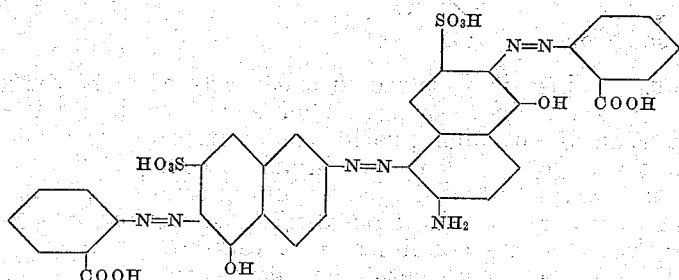
53.5 parts of the dyestuff 2:1'-azonaphthalene-5:5'-dihydroxy-2'-amino-7:7'-disulfonic acid are dissolved together with 50 parts of calcined sodium carbonate in 600 parts of water. Into this solution, at 6-8° C. there is introduced the diazo-compound from 14.4

parts of crystallized copper sulfate and after some minutes, a new dyestuff. When this is dry it is a dark powder which dissolves in water and dilute alkalis to grey solutions and dyes cotton and artificial silk uniform grey tints in a bath containing Glauber's salt and neutral or alkaline.

Example 4

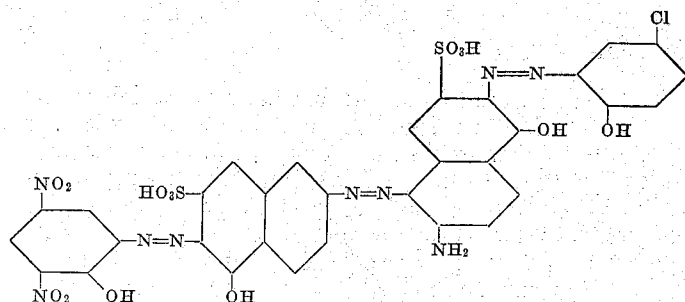
54 parts of the sodium salt of the mono-azo-dyestuff obtained in acetic acid solution from diazotized 2-amino-5-hydroxynaphthalene-7-sulfonic acid are dissolved in 600 parts of water and this solution is mixed with 55 parts of sodium carbonate. The diazo-compound from 32 parts of anthranilic acid is then added and the dyestuff formed after some time is isolated.

By boiling the dyestuff of the formula



parts of 4-chloro-2-amino-1-phenol and after some time the diazo-compound from 19.9 parts of picramic acid. After 16 hours the azo-dyestuff thus produced of the formula

thus formed with a solution of chromium fluoride containing 25 parts of Cr_2O_3 in 3000 parts of water during 15-20 hours, the chromium compound of the new dyestuff is



is filtered and dissolved in 4000 parts of hot water. There are then added 30 parts of Cr_2O_3 in the form of a chromium fluoride solution and the whole is heated for 24 hours in a reflux apparatus. The new dyestuff can be salted out with common salt. When dry it is a dark powder which dissolves in water and dilute alkalis to greenish-gray solutions and dyes cotton and artificial silk fast uniform grey tints in a bath containing Glauber's salt and neutral or alkaline with sodium carbonate.

If the azo-dyestuff is dissolved in 4000 parts of water and the solution mixed with only 7.6 parts of Cr_2O_3 in the form of chromium fluoride solution and then heated for 24 hours at the boil, there is obtained, after addition of 30

formed. When dry the same is a dark powder, dissolving in water and dilute alkalis to a violet coloration, and in concentrated sulfuric acid to a grey-blue solution. The vegetable fiber is dyed violet tints in a neutral or alkaline bath with sodium carbonate.

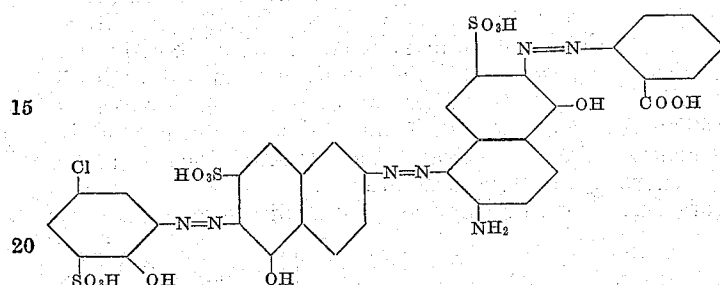
By treating the azo-dyestuff of the first paragraph of this example with a solution of 25 parts of copper sulfate and 20 parts of Cr_2O_3 in the form of chromium fluoride, there are obtained metal compounds with similar dyeing properties yielding red-violet tints.

Example 5

54 parts of the mono-azo-dyestuff obtained from diazotized 2-amino-5-hydroxynaphthalene-7-sulfonic acid and 2-amino-5-hydroxy-

naphthalene-7-sulfonic acid (acetic acid coupled) are dissolved in 500 parts of water and combined in the presence of sodium carbonate with the diazo-compound from 22.3 parts of 4-chloro-2-amino-1-phenol-6-sulfonic acid and then coupled with the diazo-compound from 15.7 parts of anthranilic acid. The dyestuff is precipitated by addition of common salt.

The dyestuff of the formula

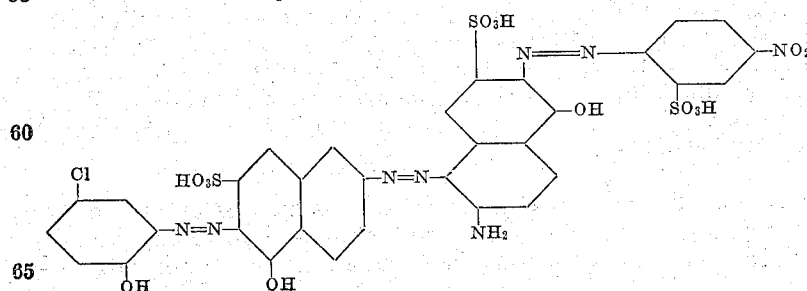


thus obtained is dissolved in 5000 parts of water and boiled during 24 hours with a solution of chromium fluoride containing 20 parts of Cr_2O_3 . The new chromium compound is then isolated by addition of common salt. It is a dark powder, dissolving in water, dilute alkalis and concentrated sulfuric acid to blue solutions and dyeing cotton and viscose grey-blue level tints.

By treating the azo-dyestuff of the first paragraph of this example with a solution of 25 parts of copper sulfate and 20 parts of Cr_2O_3 in the form of a chromium salt (fluoride, acetate), there are obtained violet or blue-violet dyeing metal compounds with similar dyeing properties as the chromium compound.

Example 6

23.9 parts of diazotized 2-amino-5-hydroxynaphthalene-7-sulfonic acid are coupled in the presence of acetic or formic acid with 23.9 parts of 2-amino-5-hydroxynaphthalene-7-sulfonic acid; when coupling is complete the solution is rendered alkaline by addition of 60 parts of sodium carbonate. It is then added to the diazo-compound from 14.3 parts of 4-chloro-2-amino-1-phenol and after this compound has disappeared, the diazo-compound from 22.5 parts of p-nitraniline-sulfonic acid is then further introduced into the solution. After a short time the whole is heated and the dyestuff of the formula

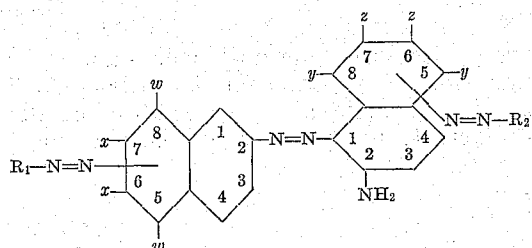


thus produced is precipitated by means of common salt. It is dissolved in 3000 parts of water and heated for 36 hours in a reflux apparatus with 15 parts of Cr_2O_3 in the form of chromium fluoride. The chromium compound is separated by addition of common salt. When dry it is a blackish powder, dissolving in water and dilute alkalis to blue solutions in concentrated sulfuric acid to a blackish-blue solution. Cotton and viscose

are dyed grey level tints in a neutral bath or in a bath made alkaline by addition of sodium carbonate.

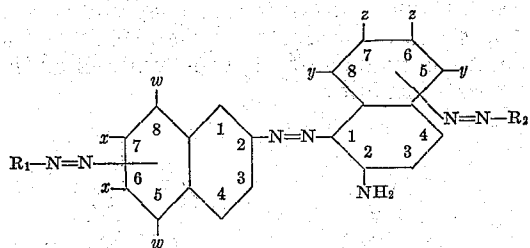
What we claim is:—

1. A manufacture of new metal compounds of azo-dyestuffs by treating a poly-azo-dyestuff of the general formula



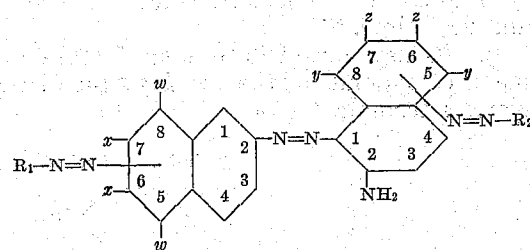
in which R_1 and R_2 are benzene radicles from which at least the one of these contains a mordant binding group in ortho-position to the $-\text{N}=\text{N}-$ group, in which one of the w 's and one of the y 's stand for an OH-group and the other w and the other y for a hydrogen atom, one of the x 's and one of the z 's represent a SO_3H -group, and the other x and the other z a hydrogen atom, the sulfo-groups being in meta-position to the OH-groups, further in which the two azo-groups are linked in ortho-position to the OH-groups, and in which at most one OH-group stands in 8-position, with a group of agents yielding metals the atomic weights of which range from 52 to 58.7.

2. A manufacture of new metal compounds of azo-dyestuffs by treating a poly-azo-dyestuff of the general formula



in which R_1 and R_2 are benzene radicles, from which at least the one of these contains a mordant binding group in ortho-position to the $-N=N-$ group, in which one of the w 's and one of the y 's stand for an OH-group and the other w and the other y for a hydrogen atom, one of the x 's and one of the z 's represent a SO_3H -group, and the other x and the other z a hydrogen atom, the sulfo-groups being in meta-position to the OH-groups, further in which the two azo-groups are linked in ortho-position to the OH-groups, and in which at most one OH-group stands in 8-position, with a group of agents yielding metals the atomic weights of which range from 52 to 58.7, together with agents yielding other metals which are capable to form with the lake-forming groups of the poly-azo-dyestuff complex metal compounds.

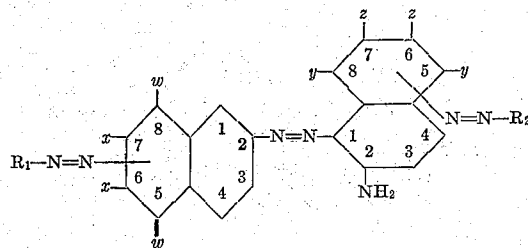
3. A manufacture of new metal compounds of azo-dyestuffs by treating a poly-azo-dyestuff of the general formula



in which R_1 and R_2 are benzene radicles, containing a mordant binding group in ortho-position to the $-N=N-$ group, in which one of the w 's and one of the y 's stand for an OH-group and the other w and the other y for a hydrogen atom, one of the x 's and one of the z 's represent a SO_3H -group, and the other x and the other z a hydrogen atom, the sulfo-groups being in meta-position to the OH-groups, further in which the two azo-groups are linked in ortho-position to the OH-groups, and in which at most one OH-group stands in 8-position, with agents yielding chromium.

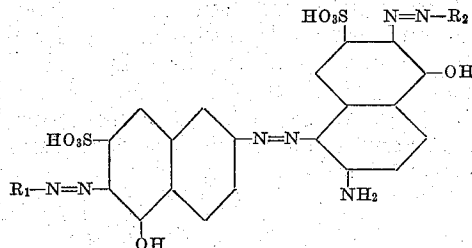
4. A manufacture of new metal com-

pounds of azo-dyestuffs by treating a poly-azo-dyestuff of the general formula



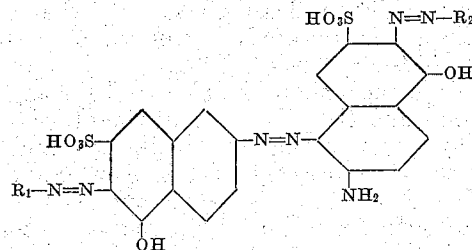
in which R_1 and R_2 are benzene radicles, containing a hydroxy-group in ortho-position to the $-N=N-$ group, in which one of the w 's and one of the y 's stand for an OH-group and the other w and the other y for a hydrogen atom, one of the x 's and one of the z 's represent a SO_3H -group, and the other x and the other z a hydrogen atom, the sulfo-groups being in meta-position to the OH-groups, further in which the two azo-groups are linked in ortho-position to the OH-groups, and in which at most one OH-group stands in 8-position, with agents yielding chromium.

5. A manufacture of new metal compounds of azo-dyestuffs by treating a poly-azo-dyestuff of the general formula



in which R_1 and R_2 are benzene radicles, containing a hydroxy-group in ortho-position to the $-N=N-$ group, with agents yielding chromium.

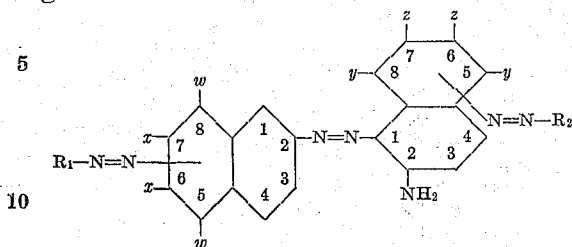
6. A manufacture of new metal compounds of azo-dyestuffs by treating a poly-azo-dyestuff of the formula



in which R_1 and R_2 are benzene radicles, containing a hydroxy-group in ortho-position to the $-N=N-$ group, with salts of the trivalent chromium.

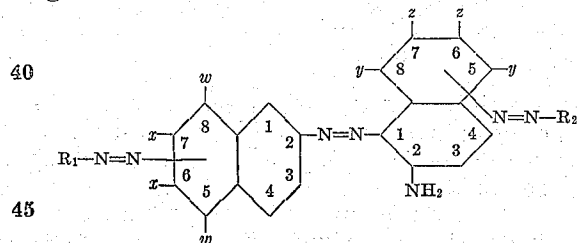
7. As new products of manufacture the metal compounds deriving from a group of metals the atomic weights of which range

from 52 to 58.7 of the azo-dyestuffs of the general formula



15 in which R_1 and R_2 are benzene radicles, from which at least the one of these contains a mordant binding group in ortho-position to the $-N=N-$ group, in which one of the w 's and one of the y 's stand for an OH-group and the other w and the other y for a hydrogen atom, one of the x 's and one of the z 's represent a SO_3H -group, and the other x and the other z a hydrogen atom, the sulfo-groups being in meta-position to the OH-groups, further in which the two azo-groups are linked in ortho-position to the OH-groups, and in which at most one OH-group stands in 8-position, which products are when dry dark colored powders, soluble in water and dilute alkalis to blue to grey-blue and grey solutions and in concentrated sulfuric acid to blackish-blue to blue and grey solutions, and dyeing vegetable fiber and especially artificial silk from so-called regenerated cellulose fast violet to blue and grey tints.

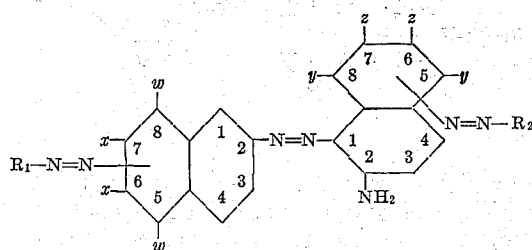
35 8. As new products of manufacture the metal compounds of the azo-dyestuffs of the general formula



50 in which R_1 and R_2 are benzene radicles, from which as least the one of these contains a mordant binding group in ortho-position to the $-N=N-$ group, in which one of the w 's and one of the y 's stand for an OH-group and the other w and the other y for a hydrogen atom, one of the x 's and one of the z 's represent a SO_3H -group, and the other x and the other z a hydrogen atom, the sulfo-groups being in meta-position to the OH-groups, further in which the two azo-groups are linked in ortho-position to the OH-groups, and in which at most one OH-group stands in 8-position, containing besides a group of metals the atomic weights of which range from 52 to 58.7 still other metals which products are when dry dark colored powders, soluble in water and dilute alkalis to blue to grey-blue and grey solu-

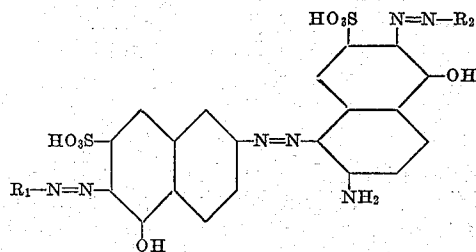
tions and in concentrated sulfuric acid to blackish-blue to blue and grey solutions, and dyeing vegetable fiber and especially artificial silk from so-called regenerated cellulose fast violet to blue and grey tints.

9. As new products of manufacture the metal compounds of the azo-dyestuffs of the general formula



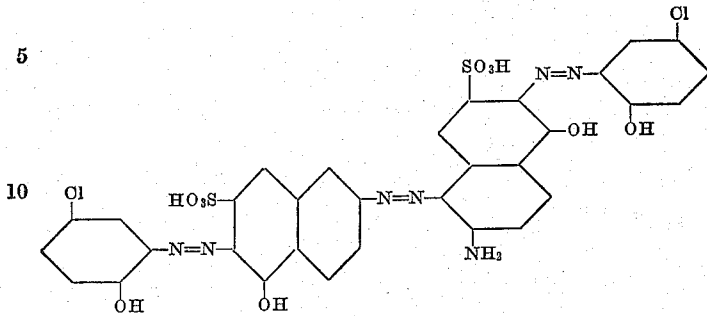
85 in which R_1 and R_2 are benzene radicles, containing a hydroxy group in ortho-position to the $-N=N-$ group, in which one of the w 's and one of the y 's stand for an OH-group and the other w and the other y for a hydrogen atom, one of the x 's and one of the z 's represent a SO_3H -group, and the other x and the other z a hydrogen atom, the sulfo-groups being in meta-position to the OH-groups, further in which the two azo-groups are linked in ortho-position to the OH-groups, and in which at most one OH-group stands in 8-position, containing chromium, which products are when dry dark colored powders, soluble in water and dilute alkalis to blue to grey-blue and grey solutions and in concentrated sulfuric acid to blackish-blue to blue and grey solutions, and dyeing vegetable fiber and especially artificial silk from so-called regenerated cellulose fast blue and grey tints.

10. As new products of manufacture the metal compounds of the azo-dyestuffs of the general formula



120 in which R_1 and R_2 are benzene radicles, containing a hydroxy-group in ortho-position to the $-N=N-$ group, which products contain chromium, forming when dry dark colored powders, soluble in water and dilute alkalis to blue to grey-blue and grey solutions, and in concentrated sulfuric acid to blackish-blue to blue and grey solutions, and dyeing vegetable fiber and especially artificial silk from so-called regenerated cellulose fast blue and grey tints.

11. As a new product of manufacture the chromium compound of the azo-dyestuff of the formula



which product forms when dry a dark colored powder, soluble in water and dilute alkalis to grey-blue solutions, in concentrated sulfuric acid to a blackish-blue solution, and dyeing vegetable fiber and especially artificial silk from so-called regenerated cellulose fast grey tints.

In witness whereof we have hereunto signed our names this 21st day of February, 1929.

FRITZ STRAUB.
WALTER ANDERAU.