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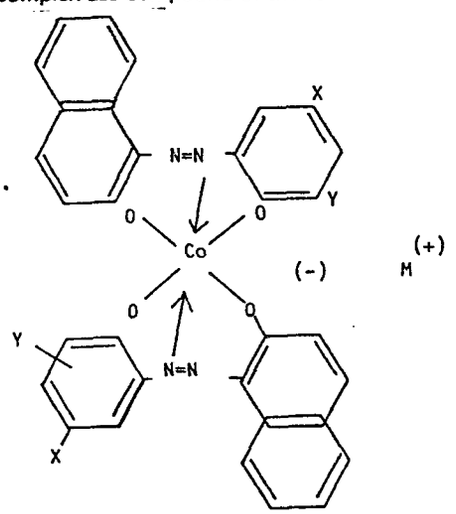
(54) **Resin composition.**

(57) A toner resin composition comprising a toner resin and a cobalt complex azo compound of the formula:



wherein $M^{(+)}$ is a cation

X & Y are each independently H, C_{1-4}-alkyl, C_{1-4}-alkoxy, halo or $-SO_2Z$

Z is C_{1-4}-alkyl, C_{1-4}-alkenyl or NRR^1 and

R & R^1 are each independently, H, C_{1-4}-alkyl, C_{1-4} alkenyl or phenyl,

and a toner composition, suitable for use in electro-reprographic processes, comprising the toner resin composition and a colorant.

Resin Composition

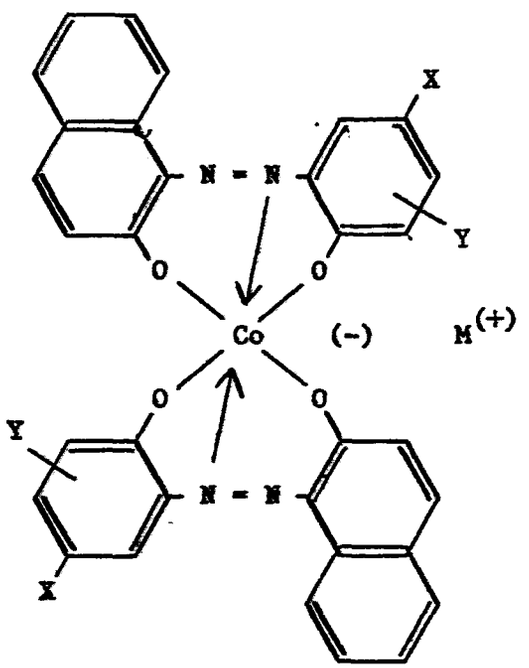
This specification describes an invention relating to a toner resin composition and a toner composition, containing a cobalt-complex of an azo dye as a charge control agent (CCA), suitable for use in electro-reprographic processes.

Traditionally, 2:1 chromium complexes of azo dyes are the most important class of metal complex dyes (see The Chemistry of Synthetic Dyes (Venkataraman), Vol III, Chap VII, "The Chemistry of Metal Complex Dyes" by R.Price & The Colours Index, 3rd Edition), one of the main reasons for their importance being their high stability compared with analogous complexes of azo dyes with other metals, such as cobalt.

This known stability of the chromium complex dyes, and their commercial availability, has led to their commercial use as charge control agents because such agents must be able to resist the processing conditions, involved in the preparation of toner compositions, i.e. hot melt kneading at temperatures from 150-200°C for several hours during dispersion into the toner resin. Typical commercial charge control agents of this type are CI Acid Black 63 (the 2:1 complex of chromium with 1-(2-hydroxy-4-nitrophenylazo)-2-hydroxy-naphthalene), the 2:1 complex of chromium with 1-(2-hydroxy-5-sulphonamidophenylazo)-2-hydroxynaphthalene and the 2:1 complex of chromium with 1-(2-hydroxy-5-chlorophenylazo)-2-hydroxynaphthalene.

It has now been surprisingly found that 2:1 cobalt complexes of certain azo dyes have particularly good properties as charge control agents in electro-reprographic toner compositions.

According to a first aspect of the present invention there is provided a toner resin composition comprising a toner resin and a cobalt complex azo compound of the formula:



I

wherein $M^{(+)}$ is a cation

X & Y are each independently H, C_{1-4}-alkyl, C_{1-4}-alkoxy, halo or $-SO_2Z$

Z is C_{1-4}-alkyl, C_{1-4}-alkenyl or NRR^1 and

R & R^1 are each independently H, C_{1-4}-alkyl, C_{1-4}-alkenyl or phenyl.

The cation, $M^{(+)}$, may be any suitable monovalent cation, such as an alkali metal, e.g. lithium, sodium or potassium, or an optionally substituted ammonium ion, e.g. NH_4^+, $(CH_3)_3NH^+$ or $(CH_3)_4N^+$ but is preferably a proton, H^+.

The halo group represented by X or Y is preferably chloro.

The alkyl, alkoxy, alkenyl or phenyl group represented by X, Y, Z, R or R^1 is preferably unsubstituted but the phenyl group may carry one or more non-ionic substituents, such as C_{1-4}-alkyl, C_{1-4}-alkoxy, halo or cyano.

The group represented by Y is preferably in one of the two positions between X and and the oxy group attached to the cobalt, i.e. in the meta or para position relative to the azo link but, more preferably, Y is meta with respect to X and with respect to the azo link.

In a preferred species of Formula I, X is chloro or $-SO_2NH_2$ and Y is H or chloro.

The toner resin is a thermoplastic resin suitable for use in the preparation of toner compositions, a preferred resin being a styrene or substituted styrene polymer or co-polymer, especially a styrene-acrylic co-polymer, such as polystyrene and styrene-butadiene or styrene-butyl methacrylate co-polymers. Other suitable resins are polyesters, especially propoxylated bis-phenol-based polyester resins, polyvinyl acetate, polyalkenes, poly(vinyl) chloride, polyurethanes, polyamides, silicones, epoxy resins, phenolics etc. Further examples of these and other resins are given in the book "Electrophotography" by R.M.Schaffert (Focal Press), UK 2,090,008A, USP 4,206,064 and USP 4,407,924.

The toner resin composition may contain, as charge control agent (CCA), more than one compound of Formula I, for example, the CCA may comprise a mixture of the compounds of Formula I in which M & Y are H & X is $-SO_2NH_2$ and M & Y are H and X is chloro. The composition desirably contains, in total, from 0.1% to 12%, preferably from 0.5% to 10% and conveniently around 2.5%, by weight, of CCA.

The toner resin composition is conveniently prepared by known methods, i.e. by kneading the molten resin with the CCA, at a temperature of 100°C or above, generally 150-200°C for several hours so that the latter becomes dispersed throughout the resin.

According to a second aspect of the present invention there is provided a toner composition comprising a resin composition as hereinbefore defined and a colorant.

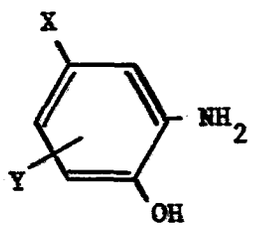
The colorant is preferably a pigment which is dispersed evenly throughout the resin phase. Examples of suitable colorants

are carbon black, phthalocyanines, metallised lakes & toners, and various azo and anthraquinone pigments.

The toner composition preferably contains not more than 20% by weight, and more preferably from 3% to 10%, of colorant.

The toner composition may be prepared by dispersing the finely-divided colorant into a dispersion of the CCA in the resin by kneading above the melting point of the resin, conveniently around 150°C for several hours so that the pigment becomes distributed throughout the resin. Alternatively, the toner resin may be mixed with the CCA and the colorant and the three components kneaded together for several hours as before. The resin is then cooled, crushed and micronised until the mean diameter of resin particles is below 20 μm and, for high resolution printing, more preferably from 1 to 10 μm.

The CCA may be conveniently prepared by (i) diazotising an amine of the formula:



wherein X and Y are as hereinbefore defined.

(ii) coupling with 2-naphthol under alkaline conditions and preferably at a reduced temperature (0-10°C), optionally followed by isolation of the azo compound using conventional techniques, such as filtration, washing and drying,

(iii) heating of the optionally isolated azo compound with a cobalt(II) salt, e.g. chloride, sulphate or acetate, in an aqueous or organic/aqueous medium at 25-100°C, preferably 60-80°C, with the slow addition of alkali, followed by heating until the metallised azo compound is formed (usually ca 6 hours),

(iv) forming the appropriate free acid or salt form of the CCA by acidification and, where necessary, addition of ammonia, an amine or a metal hydroxide, and

(v) isolation by standard techniques, such as cooling, salting, filtration, washing and drying.

The resin and toner compositions in accordance with the present invention have particularly well adapted for use in electro-reprographic processes on account of the good dispersibility of the CCA and the high charge capacity of the toner composition. The superior qualities of the compositions give rise to improved copy quality.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise indicated.

The following CCA, in accordance with Formula I, in the free acid form ($M^{(+)} = H^{+}$), were made by standard methods:

CCA A 2:1 Cobalt complex of 1-(2-hydroxy-5-aminosulphonylphenyl-azo)-2-hydroxynaphthalene (CI Acid Red 277)

CCA B 2:1 Cobalt complex of 1-(2-hydroxy-5-chlorophenylazo)-2-hydroxynaphthalene

CCA C 2:1 Cobalt complex of 1-(2-hydroxy-3,5-dichlorophenylazo)-2-hydroxy-naphthalene

CCA D 2:1 Cobalt complex of 1-(2-hydroxy-5-methylsulphonylphenyl-azo)-2-hydroxynaphthalene

CCA E 2:1 Cobalt complex of 1-(2-hydroxy-5-methylphenylazo)-2-hydroxynaphthalene

CCA F 2:1 Cobalt complex of 1-(2-hydroxy-5-[4-(ethoxy)phenyl-sulphonyl]phenylazo)-2-hydroxynaphthalene

CCA G 2:1 Cobalt complex of 1-(2-hydroxy-3-chloro-5-methylphenyl-azo)-2-hydroxynaphthalene

Example 1

A resin composition was prepared by kneading at 150°C for 30 minutes a mixture of 20g of a styrene-acrylic resin (HIMER TB1000) and 0.5g parts of CCA A. The resin composition was then cooled to

room temperature. This resin composition is hereinafter referred to as RC 1.

Examples 2 to 7

Resin compositions were prepared by the method of Example 1 using each of CCA B to CCA G described above, the Example numbers following the alphabetical order of the CCA. These compositions are hereinafter referred to as RC 2 to 7 respectively.

Example 8

The resin composition of Example 1 was converted into a toner composition by kneading 93 parts of the resin composition with 7 parts of carbon black, (ELFTEX 415) at 160°C for 3 hours, cooling and grinding the composition until the mean diameter of the particles was <20 μm. This toner composition is hereinafter referred to as TC 7.

Examples 9 to 14

Toner compositions were prepared by the method of Example 8 using the resin compositions described in Examples 2 to 7 . These toner compositions are hereinafter referred to as TC 9 to 14 respectively.

Assessment of Resin and Toner Compositions

Dispersibility of CCAs in Toner Resins

A portion of each of RC 1, RC 2 and RC 3 weas melted by heating to 150°C and a thin layer formed on a microscope slide. On cooling to room temperature the slide was examined under a microscope at a magnification of 200x. For each resin composition the particles of CCA were evenly distributed throughout the resin in the form of small spheres having a mean diameter of 3 - 5 μm, with no particles or aggregates greater than 10 μm.

Charge Capacities of Toner Compositions

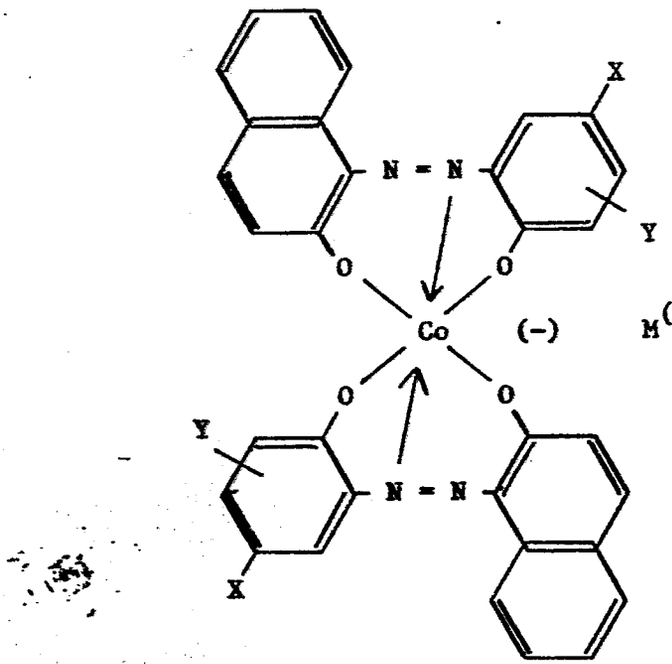
Two developers were prepared from each of toner compositions TC 8 and TC 9, containing 2% and 10% by weight of toner, by mixing 2 & 10 parts of toner composition with 98 & 90 parts of iron particles, respectively. The initial triboelectric charge (μC/g) of each of developer was determined by the standard "Blow-off" method described by Schein (J.App.Physics, 46, (1975) p 5140) using a Toshiba TB200 "Blow-off" machine. The results of these measurements are shown in Table 1.

Table 1

Toner Composition	Triboelectric Charge (μC/g)	
	2% Toner	10% Toner
8	-19.0	-14.0
9	-30.6	-21.0

CLAIMS

1. A toner resin composition comprising a toner resin and a cobalt complex azo compound of the formula:



I

wherein $M^{(+)}$ is a cation

X & Y are each independently H, C_{1-4}-alkyl, C_{1-4}-alkoxy, halo or $-SO_2Z$

Z is C_{1-4}-alkyl, C_{1-4}-alkenyl or NRR^1 and

R & R^1 are each independently H, C_{1-4}-alkyl, C_{1-4}-alkenyl or phenyl.

2. A toner resin composition according to Claim 1 wherein $M^{(+)}$ is a proton, $H^{(+)}$.

3. A toner resin composition according to Claim 1 or Claim 2 wherein the halo group represented by X or Y is chloro.

4. A toner resin composition according to any one of Claims 1 to 3 wherein Y is in the meta position with respect to X and with respect to the azo link.

5. A toner resin composition according to any one of Claims 1 to 4 wherein X is chloro or $-SO_2NH_2$.

6. A toner resin composition according to any one of Claims 1 to 5 wherein Y is H or chloro.

7. A toner resin composition according to any one of Claims 1 to 6 wherein the resin is a styrene-acrylic copolymer.

8. A toner composition comprising a toner resin composition according to any one of Claims 1 to 7 and a colorant.

9. A toner composition according to Claim 8 wherein the colorant is carbon black.