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(71) Applicant (for all designated States except US): UMICORE [BE/BE]; Rue du Marais, B-1000 Brussels (BE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): CLAUWAERT, Eddy [BE/BE]; Sint-Baafsstraat 51, B-8200 Brugge (BE).
RONDAS, Francis [BE/BE]; Binnenweg 244, B-2570 Duffel (BE).

(74) Agent: PILATE, Andre; Umicore - Patent Department, Kasteelstraat 7, B-2250 Olen (BE).

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(54) Title: MANGANESE BASED CATALYTIC DRYER FOR POLYMER COATINGS

(57) Abstract: This invention relates to catalysts for the oxidative drying of polymers, in particular for polymers used in paint or inks, based on unsaturated fatty acids, mostly from vegetal origin. A polymer compound is divulged, characterized in that it comprises a manganese-bearing alkyd polymer, said polymer compound having a manganese content of 0.5 % to 12 % by weight, a mean molecular weight of more than 2000, comprising manganese carboxylate sequences, with an acid value of less than 40 mg KOH /g, preferably of less than 20 mg KOH /g. The manganese in this polymer compound has a particularly low aqueous solubility, while the compound retains a good catalyzing activity as a drier in the target paints or inks.



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Manganese based catalytic dryer for polymer coatings

This invention relates to catalysts for the oxidative drying of polymers, in particular for polymers used in paint or inks, based on unsaturated fatty acids, mostly from vegetal origin.

Metal carboxylates are typically used as catalysts. Cobalt carboxylates are hitherto the principal and unavoidable constituents, at least if drying has to take place at room-temperature and within a reasonable time. The use of cobalt carboxylates, and in particular of cobalt octoates, has indeed been widely described, and is common practice throughout the paint industry (e.g. J.H. Bieleman, in *Additives for Coatings*, ED. J.H. Bieleman, Wiley NCH, Weinheim, 2000, p. 202). Whereas the cobalt carboxylate is the primary drier, other transition metals such as manganese also fulfill a role in this process. The effect of manganese carboxylates is most noticeable at higher temperatures, or else at room temperature when used as auxiliary drier with cobalt. The higher temperatures needed for the development of the catalytic activity of manganese as primary drier are around 80 °C, conditions normally found on printing presses, hence the use of manganese driers in these applications.

GB-A-1232194 teaches the preparation and use of acidic metal-bearing polymers in anticorrosive paints. The envisaged products have free carboxyl groups terminating the structure, which are assumed to be key in forming an adhering protective film on steel. A possible activity as drier is not mentioned, classical driers such as cobalt naphthenate being indeed added to the paint.

GB-A-550441 describes water-insoluble metal salts of polymerized rosins. This document teaches polymer salts to counter the disadvantages of existing water-insoluble non-polymerized rosins, namely their pulverulence, tendency to coalesce, and their low melting point. The reduced aqueous solubility of polymerized rosins compared to non-polymerized rosins is not taught. Moreover, the described products are not particularly alkyd-compatible as they do not contain ester functions in their structure.

Although manganese is also an essential component of life, e.g. as the central atom in SOD's (Super Oxide Dismutase), there is a known toxicology on manganese compounds.. Manganese carboxylates have not been classified as yet, but it has been demonstrated that manganese carboxylates release manganese ions in aqueous solutions. Concern about the future classification of manganese carboxylates is therefore justified.

It is known in the printing ink industry that the application of printing inks on fast running rotary printing presses causes the formation of an air borne aerosol of fine ink droplets around the printing press. The phenomenon is often called "misting". As the primary risk is therefore absorption through inhalation, it is important to lower the water solubility, and hence the release of manganese ions at the pH values typically found in lung fluids, which is around neutral.

This invention divulges a new class of manganese-bearing compounds, which retain the catalytic effects of manganese towards the oxidative drying of polymers, while greatly avoiding toxic effects by reducing the availability of the manganese ion in aqueous systems.

A first embodiment of the invention concerns a polymer compound for use as a polymerization agent in coatings, characterized in that it comprises a manganese-bearing polymer, said polymer compound having a manganese content of 0.5 % to 12 % by weight, a mean molecular weight of more than 2000, comprising manganese carboxylate sequences, with an acid value of less than 40 mg KOH /g, preferably of less than 20 mg KOH /g.

It is to be noted that any polymer compound "for use as a polymerization agent", has implicitly to be at least partially soluble in the targeted paints or inks, which are typically based on organic compounds, in particular on oils such as vegetable oils.

The mean molecular weight can be estimated from the remaining free functionalities of the polymer, or by any appropriate analytical technique.

Fatty acids are the preferred carboxylic acids, as such alkyd type polymers are more compatible with the alkyd binders used in paints and inks. For the same reason, the polymer could have an excess of hydroxyl groups.

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The polymer compound should preferably have a manganese content of between 1 and 6 % by weight. Also, a mean molecular weight of more than 3000 is preferred to further limit the aqueous solubility of the metal. It may be unsaturated to increase its solubility in unsaturated binders for paints or inks, and to participate in the drying process not only as a catalyst. The polymer compound should ideally be completely soluble in printing ink media such as hydrocarbon or alkyd resins, or any mixture thereof. To this end, it is advisable to prefer polymer compounds having a mean molecular weight of less than 250000.

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15 The manganese atoms can be an integral part of the backbone chain of the polymer. By this is meant that the manganese atoms form links in the backbone chain of polymers. Such integrally bound manganese indeed imparts its full catalytic effect to the polymer, while its water solubility is greatly suppressed.

20 The polymer compound should preferably be free of P, N and S. These elements are generally to be avoided in the considered catalysts, as they bear a negative effect on the drying capacity of the paints or inks. They may moreover generate noxious combustion gasses when the coated articles or materials are recycled.

25 In next embodiment, a drier composition is provided as a solution comprising the above-described polymer compound; hexylene glycol is a suitable solvent.

In a next embodiment, the polymer compound is used as a polymerization agent in a polymer-based coating formulation.

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In a next embodiment, a polymer-based coating formulation is provided, comprising a binder and the polymer compound. Optionally, a cobalt-bearing compound can be added to the formulation, such as a cobalt carboxylate or a polymeric cobalt carboxylate. The binder can preferably comprise an unsaturated fatty acid modified polymer. The polymer compound may be adapted so as to co-polymerize with this binder. The polymer-based coating formulation preferably has a manganese content of 0.01 % to 0.5 % by weight on binder.

The last embodiment of the invention is related to the process for the preparation of the polymer compounds. This process comprises the steps of reacting a manganese salt or oxide, preferably manganese acetate, with an acid functional polymer, or with a mixture of polybasic and monobasic carboxylic acids, thereby obtaining a first intermediate compound; and, of reacting said first intermediate compound with a polyol, or a mixture of polyols, until water evolution ceases.

Suitable divalent carboxylic acids are dimeric fatty acids, orthophthalic acid, isophthalic acid, terephthalic acid, maleic acid, adipic acid, succinic acid, sebacic acid, dodecanoic acid, or any mixture thereof.

Optionally, monobasic acids are added, such as a saturated or unsaturated fatty acid after reaction with dienes, neodecanoic acid, naphthenic acid, isononanoic acid, stearic acid, or any mixture thereof.

Suitable polyols are glycerol, pentaerythritol, dipentaerythritol, synthetic polyols, or any mixture thereof.

The reactants are reacted in such proportions that there is preferably a small excess of basic constituents, which results in a limited amount of free hydroxyl functionality. This tends to insure a good solubility in the binder formulation. Generally, but not exclusively, the manganese compound is first reacted with an excess of the carboxylic acids, resulting in a lower molecular weight manganese bearing compound with excess carboxylic

functionality, which is then further reacted with one or more polyols to the final macromolecular structure.

This reaction scheme is applicable to any multivalent metal that can be obtained in a reactive form. Metals such as Ce, Zr, V, Sr, and Pb can be considered.

Example 1

This example illustrates the synthesis of the polymer compound, its composition, solubility, and activity as a drier.

Synthesis

In a round bottomed glass reaction vessel, equipped with a stirrer, inlets for liquid and solid reactants, an inlet for inert gas, temperature control, an outlet for gaseous reaction products, are introduced 200 g of dimeric fatty acids and 600 g of dehydrated castor oil fatty acids. Thereafter, at a temperature of 100 °C and under nitrogen, 175 g of manganese acetate tetrahydrate are slowly added under vigorous stirring, allowing the reaction by-products water and acetic acid to escape.. The reaction is assumed to be terminated when no more water or acetic acid is evaporating from the reaction mix at a temperature of 110 °C.

200 g of xylene are then added and the temperature is raised to 145 °C. The reaction vessel is equipped with a water/xylene separator so as to return the boiled-off xylene to the reaction vessel. Further xylene is added so as to obtain a constant reflux stream of xylene at a temperature of 160 °C.

88 g of glycerol are prepared in a fitting dropping funnel and are added slowly to the reaction mix. Care is taken to obtain a good separation of the reaction water. As the viscosity of the reaction mix increases during reaction, the temperature is raised to maintain the reaction mix stirrable. The final reaction temperature is 200 °C.

When all glycerol has been added, and when no more reaction water is formed, the temperature is maintained for another two hours to finalize of the reaction. The product is then vacuum distilled, down to about 15 Torr. The temperature is allowed to drop down to 180 °C.

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A very viscous brown colored mass is obtained. This product is dissolved in 150 g of hexylene glycol, and allowed to cool to ambient temperature.

Composition and molecular weight

10 The final product is a brown clear liquid with the following basic properties:

- manganese content 3.62 %;
- non volatile content 85.5 %;
- viscosity 13.8 Pa·s at 25 °C.

15 This original manganese content of the synthesized polymer compound before dissolution is 4.23 %.

The compound of the example is analyzed using a Varian GPC. A sample of the obtained product is diluted in THF, a standard solvent for this kind of analysis, and a chromatogram
20 is obtained using a polystyrene column and a refractive index type of detector. The mean molecular weight of the synthesized polymer compound amounts to 4000 Dalton.

The performances of the obtained products, in terms of aqueous solubility, and as a drier,
25 are illustrated below.

Aqueous solubility

The water solubility of the compound from the example is determined by the standard test according to the procedure described in OECD 105. In this procedure a sample weight
30 chosen so as to produce a saturated aqueous solution is ground to a fine powder and shaken with distilled water at a temperature of 30 °C. After 24 hours this suspension is

allowed to cool to 20 °C and kept at this temperature during 24 more hours. After filtration, the manganese concentration in the filtrate is determined by atomic absorption spectrometry. The solubility of the polymeric manganese compound is found to be less than 0.5 mg Mn/l. This figure is considered excellent.

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This same test is also performed on manganese octoate, a reference drier in common use in the paint and printing ink industry. The solubility of the reference octoate amounts to 140 mg Mn/l.

10 Drier activity

Manganese is considered to be a primary drier at elevated temperatures only. It has however also shown useful at room temperature when combined with cobalt-based driers.

For the evaluation of the drying activity of the invented polymer compounds, a drying test with a standard alkyd resin is performed, namely Umicore's alkyd resin Valires[®] RE 170.06, a long soybean oil alkyd supplied at 70 % non volatile content, a typical value for a standard solvent borne decorative paint. The alkyd is first diluted to 60 % non volatile content with an aromatic free petroleum distillate (Exxsol[®] D40), and then the driers are added.

20

For the driers, combinations with standard calcium and zirconium carboxylates as auxiliary driers are chosen. An additional combination is prepared as a mixture of cobalt carboxylate with the polymer compound according to this example. The driers are mixed with the alkyd resin, resulting in the paint formulations shown in Table 1.

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Table 1: Paint formulations

Formulation	Ca (%)	Zr (%)	Co (%)	Mn (%)	Mn compound
1a	0.2	0.1	-	0.025	Example 1
1b (*)	0.2	0.1	-	0.025	Octoate
2a	0.2	0.1	-	0.050	Example 1
2b (*)	0.2	0.1	-	0.050	Octoate
3	-	-	0.025	0.025	Example 1

(*) Comparative

The different paints are applied with a doctor blade on a glass plate. The wet layer thickness is 75 μm . The drying temperature is 20 °C, and the relative air humidity 60-70 %. The drying process is monitored with a Braive drying time recorder running at 3 cm/h, with needle tips of 3 mm and a net weight of 10 g. The different drying times are reported in Table 2.

10 Table 2: Drying times

Formulation	Solvent evaporation (h)	Dust free (h)	Through dry (h)
1a	0.33	13.1	15.5
1b (*)	0.32	19.1	24.3
2a	0.43	17.0	19.7
2b (*)	0.45	20.3	24.0
3	0.18	5.17	11.10

(*) Comparative

It appears that of 0.025 % Mn on alkyd resin solids is a sufficient or even optimal amount. The results show a clear advantage of using the polymeric manganese compound, a result that is assumed to stem from the co-polymerization of the compounds with the alkyd resin. Manganese octoate indeed remains as a foreign substance in the final composition.

The result of the manganese-cobalt combination shows even faster drying times, in line with the requirements of the paint industry for air drying alkyd systems.

5 Example 2

This example illustrates the importance of the excess basic functionality of the polymers.

To demonstrate this effect, the synthesis of Example 1 is repeated adding different levels of excess organic acid during synthesis. In this case, the chosen organic acid is 2-ethylhexanoic acid. The results are shown in Table 3. The aqueous solubility tests are according to OECD 105, as in Example 1.

Table 3: Increasing Mn solubility when excess acid is used during synthesis

Added acid (%)	Mn (%)	Aqueous solubility (mg/l)	Acid value (mg KOH/g)
- (*)	4.23	0.5	0
7.5	3.96	7	23
10	3.85	8	30
22	3.61	46	56

(*) According to Example 1

15

It can be seen that the aqueous solubility increases with the acid value of the polymer. Although still acceptable, a solubility of less than 50 mg/l of Mn is recommended. To this end, an acid value of less than 40 mg KOH/g is preferred, this value giving some margin even when polymers other than those of Example 1 are considered. This contrasts with prior art such as GB-A-1232194 describing metal-containing acidic polymers for use in rust-proofing applications.

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Claims

1. Polymer compound for use as a polymerization agent in coatings, characterized in that it comprises a manganese-bearing alkyd polymer, said polymer compound having a
5 manganese content of 0.5 % to 12 % by weight, a mean molecular weight of more than 2000, comprising manganese carboxylate sequences, with an acid value of less than 40 mg KOH /g, preferably of less than 20 mg KOH /g.
2. Polymer compound according to claim 1, characterized in that the polymer is
10 neutral or has a hydroxyl excess.
3. Polymer compound according to claims 1 or 2, characterized in that at least part of the dibasic carboxylic acids is unsaturated dimeric acids derived from naturally occurring fatty acids.
15
4. Polymer compound according to any one of claims 1 to 3, characterized in a manganese content of 1 % to 6 % by weight.
5. Polymer compound according to any one of claims 1 to 4, characterized in that the
20 polymer has a mean molecular weight of more than 3000.
6. Polymer compound according to any one of claims 1 to 5, characterized in that the polymer is unsaturated.
- 25 7. Polymer compound according to any one of claims 1 to 6, characterized in that the polymer is soluble in printing ink media such as hydrocarbon or alkyd resins, or any mixture thereof.
8. Polymer compound according to any one of claims 1 to 7, characterized in that the
30 manganese atoms are an integral part of the backbone chain of the polymer.

9. Polymer compound according to any one of claims 1 to 8, characterized in that the polymer is essentially free of P, N and S.

10. Drier composition comprising the polymer compound according to any one of the
5 claims 1 to 9 dissolved in a solvent being preferably hexylene glycol.

11. Use of the polymer compound according to any one of claims 1 to 9 as a polymerization agent in a polymer-based coating formulation.

10 12. Polymer-based coating formulation comprising a binder and the polymer compound according to any one of claims 1 to 9.

13. Polymer-based coating formulation comprising a binder, the polymer compound according to claims 1 to 9, and a cobalt bearing compound.

15

14. Polymer-based coating formulation according to claims 12 or 13, characterized in that the binder comprises an unsaturated fatty acid modified polymer.

15. Polymer-based coating formulation according to any one of claims 12 to 14,
20 characterized in that said polymer compound is adapted so as to co-polymerize with the binder.

16. Polymer-based coating formulation according to any one of claims 12 to 15, characterized by a manganese content of 0.01 % to 0.5 % by weight on binder.

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2011/060713

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08G63/68 C09D167/08
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G C09D C09F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 014 729 A1 (SICPA HOLDING SA [CH]) 14 January 2009 (2009-01-14) paragraph [0018] - paragraph [0056] ; claims 5, 6; examples A2, A3, C, New agent V/Mn/Zr; tabl e 1	1-16
A	----- GB 1 232 194 A ((KAPA) KANSAI PAINT co LTD) 19 May 1971 (1971-05-19) page 2, line 33 - page 2, line 109 ; examples 5, 70; tabl es 2, 14 -----	1-16



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040,
 Fax: (+31-70) 340-3016

Authorized officer

Enescu, Cri sti na

INTERNATIONAL SEARCH REPORT

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