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(54) Intumescent coating composition

(57) An intumescent composition suitable for use as a coating comprises as essential components:-
(A) a chlorinated polymer which is a chlorinated rubber or a chlorinated polyalkylene,
(B) a phenol-formaldehyde novalak resin and
(C) a plasticiser for the chlorinated polymer which is a chlorinated plasticiser or a phosphorous-containing plasticiser.
The composition forms flexible, glossy coatings which are relatively water insoluble.

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SPECIFICATION

Intumescent coating composition

The present invention relates to an intumescent composition suitable for coating substrates particularly metal substrates.

Conventional intumescent coating compositions typically contain relatively high proportions of intumescent pigments dispersed in a binder. Coatings formed from such compositions are generally hard, brittle, matt and porous. Many of the known intumescent materials are water soluble or water sensitive and so the coatings are only suitable for use in areas where they will not be exposed to moisture.

The present invention relates to a flexible, glossy composition, suitable for use as a coating composition, which has intumescent properties and is relatively water insoluble.

Thus according to the present invention an intumescent coating composition comprises as essential components.

(A) a chlorinated polymer which is a chlorinated rubber or a chlorinated polyalkylene,

(B) a phenol-formaldehyde novolak resin and

(C) a plasticiser for the chlorinated polymer which is a chlorinated plasticiser or a phosphorous-containing plasticiser.

Preferably, the proportions of the essential components of the intumescent composition are as follows:

	Parts by weight
Chlorinated polymer	40 to 90 more preferably 60 to 80
Phenol-formaldehyde novolak resin	5 to 55 more preferably 10 to 30
Plasticiser	5 to 25 more preferably 10 to 20

The ratio of chlorinated polymer to phenol-formaldehyde novolak resin is preferably at least 1:1 and is more preferably in the range 1:1 to 5:1.

Chlorinated polymers suitable for use in the present invention are known. The number average molecular weight of the chlorinated polymer is preferably in the range 10,000 to 100,000 and the chlorine content is preferably from 30 to 70% by weight. Suitable chlorinated polymers include chlorinated synthetic rubber, chlorinated polyethylene and chlorinated polypropylene. Chlorinated synthetic rubbers suitable for use in the present invention are commercially available. For example, chlorinated polyisoprene and polybutadiene having chlorine contents of from 60 to 65% by weight are sold by Imperial Chemicals Industries Limited under the registered trade mark "Alloprene". Chlorinated polyethylene and chlorinated polypropylene are commercially available from Sanyo Kokusaku Pulp Company Limited under the trade mark "Superchlon". These chlorinated polymers have chlorine contents in the range 40 to 65% by weight.

Phenol-formaldehyde novolak resins are known and may be prepared using conventional methods. Preferably, the phenol used to produce the resin is a substituted phenol, the substituent group being a C_1 to C_{10} alkyl group which is preferably branched. A para-isobutyl phenol-formaldehyde novolak resin suitable for use in the present invention is commercially available from Bakelite under the trade designation R14634/1. Chlorinated or phosphorous-containing plasticisers suitable for plasticising chlorinated polymers are known. The chlorinated plasticisers typically have a molecular weight of from 400 to 1200 and contain from 30 to 70% by weight of chlorine. Suitable plasticisers include the chlorinated paraffin waxes which are commercially available from Imperial Chemical Industries Limited under the registered trade mark "Cereclor". The phosphorous-containing plasticisers may be, for example, an alkyl or aryl phosphate or phosphite. Suitable phosphorous-containing plasticisers include triphenyl phosphites, triphenyl phosphates, tricresyl phosphates and alkyl phenyl phosphates. Isopropylated phenyl phosphate is a suitable plasticiser and is commercially available from Ciba Geigy under the trade mark "Reofos".

The essential components of the intumescent composition according to the invention are preferably dissolved or dispersed in a suitable solvent or solvent mixture, e.g. xylene or toluene, to form a coating composition. The coating composition may be applied to substrates by conventional methods such as brushing, applying with a doctor blade or casting. Typically, the solvent will comprise from 40 to 150 parts by weight per hundred parts by weight of the essential components.

When subjected to a temperature in excess of 150°C, the compositions according to the present invention intumesce to form a relatively hard, foamed char having a volume from 2 to 20 times larger than the original volume of the coating composition.

Relatively large amounts of hydrogen chloride are produced as the chlorinated rubber decomposes at high temperatures. The hydrogen chloride assists in foaming the char. However, high emissions of hydrogen chloride from the coating composition are undesirable and may be reduced by the inclusion in the coating of certain finely divided fillers which react with the hydrogen chloride. Preferably the reaction between the hydrogen chloride and the filler results in the evolution of another gas or vapour e.g. carbon dioxide or water. Suitable fillers include calcium carbonate, magnesium carbonate, alumina trihydrate and zinc borate.

The amount of filler is preferably in the range 10 to 40% and more preferably 15 to 25% by weight based on the total weight of filler and the essential components. Preferably the filler has an average particle size of less than 10 microns. Finely divided calcium carbonate alone or in combination with magnesium oxide is the preferred filler. The magnesium oxide may be added as a finely divided filler and/or thermal stabiliser. It may be reacted with the phenol-formaldehyde novolak resin before the essential components are mixed together.

Magnesium ammonium phosphate may be included in the compositions to thermally stabilise the char and also to assist the foaming of the char. Other thermal stabilisers include, for example, magnesium oxide, melamine phosphate may be included in the compositions in an amount up to 25 parts by weight per hundred parts of the essential components and the other thermal stabilisers in amounts of up to 10 parts by weight per hundred parts of the essential components without the need for any other change in the composition. However, if the thermal stabilisers are used in greater amounts a conventional blowing agent may be required. Such a blowing agent may be included in any case to improve the foaming characteristics of the char. The blowing agent selected should be relatively insoluble in and not reactive with water. A suitable conventional blowing agent is, for example, p, p^1-oxybis (benzene sulphonyl hydrazide). Increasing the amount of the phosphate thermal stabilisers, e.g. melamine phosphate, improves the properties of the char formed when the composition is subjected to a high temperature but may require the inclusion of additional carbonific material. A suitable additional carbonific has been found to be hydrophobic starch. Hydrophobic starches are known and some are commercially available. For example a silane treated starch is sold by Spillers Company Limited.

Other additives may be included in the compositions such as, for example, pigments, e.g. titanium dioxide, a stabiliser for pigment dispersions, e.g. zinc naphthenate and a thickener e.g. the castor oil based thickener sold under the trade mark "Thixomen" by Imperial Chemical Industries Limited. The thickener is particularly useful for forming viscous compositions capable of being applied as relatively thick coatings.

The total amount of fillers and other additives is preferably less than the total weight of the essential components and is more preferably less than 60 parts by weight per hundred parts by weight of the essential components.

The compositions according to the present invention may be prepared using conventional methods. Conveniently, the chlorinated polymer and the phenol-formaldehyde novolak resin are dissolved in a suitable solvent and then the other components and additives are added to and mixed with the solution. High speed mixing may be used to incorporate finely divided fillers and pigments into the composition. Larger particles may be ground by conventional techniques such as ball milling, grinding e.g. in a paint mill. The components may be mixed together at room temperature e.g. approximately 20°C. However, milling tends to increase the temperature e.g. to 50°C.

The present invention is illustrated by the following examples:

Example 1

An intumescent coating composition was prepared by mixing together the following components at a temperature of 50°C;

Component	*Amounts (parts by weight)*
Chlorinated synthetic rubber (Alloprene R20 ex ICI)	72
Chlorinated paraffin wax (Cereclor S63 ex ICI)	10
Iso butyl substituted phenol-formaldehyde novalak resin (R 14634/1 ex Bakelite)	18
Xylene	90
Castor oil based thickening agent ("Thixomen" ex ICI)	1

The chlorinated synthetic rubber had a molecular weight, Mv, as determined from the viscosity of 20g of the polymer in 100g of toluene, of 75000 and a molecular weight, Mn, as determined by vapour phase osmometry, of 88000. The chlorine content was at least 60% by weight and the density was 1.6g cm^{-3}.

A 3 mm thick film of the composition was cast onto 152 × 126 mm mild steel panels by placing the metal panel in the bottom of a 5 mm deep mould and then filling the mould with the composition. The coated panels were dried at ambient temperature (about 22°C) for 7 days.

One of the coated panels was positioned such that the longer side of the panel was at an angle of about 45° to the horizontal with the coated surface directed upwards. A Bunsen burner flame was then directed, horizontally, towards the lower part of the coated surface. A temperature probe was positioned at the centre of the lower, untreated surface of the panel. Within 45 seconds, the coating in the region of flame impingement charred and started to expand. Some smoke was given off, but the coating did not support combustion. As heating continued, the foamed area gradually expanded to a thickness of approximately 3 cms. After heating for 30 minutes, the recorded temperature was only 99°C.

For comparison a mild steel panel which had not been coated with the composition was subjected to the same test. The temperature aeasured at the lower surface of the panel rose rapidly (i.e. in less than 15 mins) to 500°C. The results show that the composition according to the present invention is capable of retarding the rate of rise in temperature of the metal substrate to which it is applied.

A thin film of the composition having an average thickness of 0.66 μm was applied to 152 × 126 mm mild steel panels using a doctor blade. The panels were dried for seven days at ambient temperature. The Ericksen Hardness of the dried coating was 50g. The coated panels were then subjected to tests to assess the water stability, wear properties and flexibility of the coatings.

A coated panel was immersed in water at 40°C for 16 hours. There was no loss in weight of the coating and the immersion had no apparent affect on the coating. This indicates that the coating is relatively water stable.

A coated panel was subjected to a scrubbing test according to ASTM D2486. This test comprises scrubbing the coating with a nylon brush at the rate of approximately 3000 cycles per hour. The coating was subjected to approximately 20 000 cycles while water was sprayed onto the surface of the coating. There was no substantial weight loss which indicates that the coating is relatively hard wearing.

The coating composition passed the conical Mandrel Test ASTM D522-60 which indicates that the coating is relatively flexible.

Example 2

An intumescent coating composition was prepared by mixing together the following components;

Component	*Amount (parts by weight)*
Chlorinated synthetic rubber ("Alloprene" R20 ex ICI)	44
Phosphated plasticiser ("Reofos" 95 ex Ciba Geigy)	7
Iso-butyl substituted phenol-formaldehyde resin (R 14634/1 ex Bakelite)	11
Magnesium oxide	8
Titanium dioxide	8
Calcium carbonate (particle size less than 10 microns)	20
Xylene	80

The phosphated plasticiser was an isopropylated phenyl phosphate.

The rubber and resin were first dissolved in the xylene and then the other materials were added and the mixture milled until the average particle size was less than 25 micron. 1 part by weight of Thixomen ex ICI was then mixed with the composition to give a viscous gel. A doctor blade was used to apply the composition to 152 × 126 mm mild steel panels to an average film thickness of 2 mm. The coated panels were then dried at ambient temperature (about 22°C) for seven days. After drying the average film thickness was about 1.3 mm and the Erickson Hardness of the coating was 200g.

Coated panels subjected to the Bunsen burner test described in Example 1 reached a temperature of 200°C after 30 minutes. The coating intumesced to form a firm char. Immersion of a coated steel panel in water at 40°C for 16 hours did not adversely affect the coating and there was no significant weight loss. The coating composition passed the Conical Mandrel Test ASTM D522-60 and there was no significant weight loss in the Scrub Test ASTM D2486.

Examples 3 to 6

Four compositions according to the present invention were prepared by mixing fillers and other additives with the composition of Example 1. The proportions of the fillers and additives included in the compositions are given in Table 1 as parts by weight per hundred parts by weight of the total weight of the composition excluding solvent.

The compositions were applied to 152 × 126 mm mild steel panels to give coatings of the thicknesses given in Table 1. Each of the panels was then subjected to the Bunsen burner insulation test as described in Example 1 and the temperatures of the lower surface of the panels after 10 mins and 30 mins are given in Table 1. These results show that the compositions according to the invention substantially retard the rate of the rise in temperature as compared with an untreated panel. The chars formed were all micro-cellular, integral chars which did not support combustion. The char thicknesses given in Table 1 indicate expansion ratios of from 3 to 19.

TABLE 1

Filler/Additive	*Example*					
(parts by wt. per 100 parts of the total weight excluding solvent)	3	4	5	6	Untreated Panel	
$CaCO_3$				20		
TiO_2		6	6	9		
MgO		6	8	8		
$Al_2O_3.3H_2O$	30					
Ammonium polyphosphate		20				
"Genitron" OB		2				
$MgNH_3PO_4.6H_2O$			21.5			
Coating thickness (mm)	3.3	2.4	4	1.1		
Insulation Test Temperatures (°C)						
10 min	158	186	124	200	498	
30 min	173	210	130	200	500	
Char Thickness (mm)	20	-	40	20		

CLAIMS

1. An intumescent composition comprising as essential components;
(A) a chlorinated polymer which is a chlorinated rubber or a chlorinated polyalkylene,
(B) a phenol-formaldehyde novolak resin and
(C) a plasticiser for the chlorinated polymer which is a chlorinated plasticiser or a phosphorous-containing plasticiser.

2. A composition as claimed in claim 1 in which the proportions of the essential components are as follows;
(A) 40 to 90 parts by weight of the chlorinated polymer,
(B) 5 to 55 parts by weight of the phenol-formaldehyde novolak resin
(C) 5 to 25 parts by weight of the plasticiser and the ratio of the chlorinated polymer to the phenol-formaldehyde resin is at least 1:1.

3. A composition as claimed in claim 2 in which the proportions of the essential components are as follows;
(A) 60 to 80 parts by weight of the chlorinated polymer,
(B) 10 to 30 parts by weight of the phenol-formaldehyde novolak resin
(C) 10 to 20 parts by weight of the plasticiser.

4. A composition as claimed in any of claims 1 to 3 in which the ratio of chlorinated polymer to phenol-formaldehyde novolak resin is in the range 1:1 to 5:1.

5. A composition as claimed in any of claims 1 to 4 in which the chlorinated polymer has a number average molecular weight of from 10,000 to 100,000 and a chlorine content of from 30 to 70% by weight.

6. A composition as claimed in any of claims 1 to 5 in which the chlorinated polymer is a chlorinated synthetic rubber having a chlorine content of from 60 to 65% by weight.

7. A composition as claimed in any of claims 1 to 6 in which the phenol-formaldehyde novolak resin is prepared from a phenol substituted with a C_1 to C_{10} alkyl group.

8. A composition as claimed in claim 7 in which the phenol is substituted with a branched chain alkyl group.

9. A composition as claimed in claim 8 in which the alkyl substituted phenol is p-isobutyl-phenol.

10. A composition as claimed in any of claims 1 to 9 in which the plasticiser is selected from the group comprising a chlorinated paraffin wax having a molecular weight of from 400 to 1200 and a chlorine content of from 30 to 70% by weight, triphenyl phosphites, triphenyl phosphates, tricresyl phosphates, and alkyl phenyl phosphates.

11. A composition as claimed in any of claims 1 to 10 in which the essential components are dissolved or dispersed in a solvent, the amount of solvent being from 40 to 150 parts by weight per hundred parts by weight of the essential components.

12. A composition as claimed in any of claims 1 to 11 which also comprises from 10 to 40% by weight of a filler based on the total weight of filler and the essential components.

13. A composition as claimed in claim 12 in which the filler is selected from the group comprising calcium carbonate, alumina trihydrate and zinc borate and has an average particle size of less than 10 microns.

14. A composition as claimed in claim 12 or claim 13 comprising from 15 to 25% by weight of filler.

15. A composition as claimed in any of claims 1 to 12 which also comprises magnesium ammonium phosphate, magnesium oxide, melamine phosphate or ammonium polyphosphate as thermal stabilisers.

16. A composition as claimed in any of claims 12 to 14 in which the total amount of fillers and other additives is less than the total weight of the essential components.

17. A composition as claimed in claim 15 in which the total amount of fillers and other additives is less than 60 parts by weight per hundred parts of the essential components.

18. A composition substantially as described with reference to the Examples.

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