

SPECIFICATION**Heat recoverable article bearing a temperature indicating composition**

This invention relates to heat recoverable articles bearing temperature indicating compositions, such compositions preferably being in the form of coating compositions, such as paints, and markers
5 such as crayons.

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Temperature indicating, or thermochromic, materials are those which change colour on being heated to a typical usually well-defined, temperature. The change in colour is frequency reversible and associated with a reversible chemical change which occurs at that temperature. Such materials are discussed and reviewed, for example, in two articles by Jess. He. Day in Chem. Rev. 63, 65 (1963) and
10 Chem. Rev. 68, 649 (1968).

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Typically thermochromic materials are used as warning indicators that a certain maximum safety temperature has been reached or as means whereby a subsequent check will reveal that some critical temperature was attained; they have also found use in desk thermometers where different materials indicate different temperatures.

15 One especially interesting application of thermochromic materials has been in the field of heat-recoverable articles such as the heat-shrinkable polymeric sleeves described and claimed in U.S. Patents Nos. 2,027,962; 3,086,242 and 3,957,372 and the heat-shrinkable wraparound sleeves described and claimed in U.S. Patent No. 3,379,218 and British Patents Nos. 1,155,470; 1,211,988 and 1,346,479. Another type of heat-recoverable article is described in British Patent No. 1,440,524 in
20 which an elastomer member such as an outer tubular member is "held out" in a stretched state by a second member, such as an inner tubular member, which upon heating weakens and thus allows the elastomeric member to recover.

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These heat-recoverable articles are typically provided with a sealant coating, for example on the inner surface of a heat-shrinkable sleeve, so that a seal is made between the sleeve and a substrate
25 such as a pipe or cable when the sleeve shrinks around it. The sealants are usually mastics or hot-melt adhesives, for example those described and claimed in British Patent No. 1,440,810 and German OS 2,723,116. In such cases, heat is required both to shrink the expanded plastics material and to melt the sealant. The heating means is often simply a torch which may degrade the plastic if it becomes too hot and yet, on the other hand, it is important that sufficient heat is applied to cause the sealant to melt
30 and flow when in contact with the substrate. It has been proposed therefore in, for example, U.S. Patent No. 3,816,335 and British Patent No. 1,511,053, to use a suitable thermochromic paint on the surface of the heat-recoverable article in order to monitor and control the heat during recovery.

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The use of these materials has been successful but those so far proposed have been inorganic in nature, which may occasionally be environmentally undesirable, and they have in general also exhibited
35 a reversible colour change. This has caused some problems in applications where a check is made some time after recovery to ensure that the heat-recoverable device was heated to the correct temperature. A further problem has been that the basic (i.e. low temperature) colour of the inorganic thermochromic substance has clashed with design and/or coding requirements.

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The present invention provides a heat-recoverable article which is to be heated to a pre-selected
40 temperature during installation or use, which is capable of forming an enclosure about a body, which carries on a surface which will face the interior of the enclosure a meltable composition, and which carries a temperature indicating composition on a surface which will be visible when the article is enclosing the body, the temperature indicating composition comprising decomposable organic material which, on heating of the article to the pre-selected temperature melts and decomposes
45 substantially irreversibly to provide a visible colour change, said pre-selected temperature being a temperature which results in the melting of said meltable composition to effect sealing of the enclosure. We have found that temperature-indicating compositions which are satisfactory for use on heat-recoverable materials can be based, according to the present invention, on surprisingly simple and inexpensive organic materials which decompose at or about their melting point. As will be explained in
50 more detail hereinafter the materials are, in some respects, not classically "thermochromic" insofar as the colour change is generally irreversible. However, for convenience, they will hereinafter be referred to as thermochromic materials.

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The essence of the present invention is that the thermochromic ingredient melts and decomposes on heating to a certain temperature (or narrow temperature range) and yields a decomposition product
55 which has a different colour. In addition, on melting, a change in refractive index usually occurs which usefully acts as an indication of the onset of the substantially irreversible colour change.

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One advantage of using such materials is that they may themselves be virtually colourless thus allowing the use of conventional pigments for colouration and, for example, of fluorescent and/or phosphorescent substances for specific design purposes.

60 The substances preferably decompose at a temperature which is not more than 10°C, preferably not more than 5°C above the melting point. Given this concept, those skilled in the art will readily be able to choose suitable low-cost, non-toxic and, often, naturally-occurring materials for any given temperature. However, for heat-recoverable articles the temperature range of interest is typically from about 60°C or 80°C to 400°C, advantageously from 180°C to 300°C, and the materials listed in the

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following Table have been found to be especially useful, the relevant decomposition temperature being indicated. Those compounds marked with a cross are thought to be most advantageous and, in particular, allantoin (white to black), ascorbic acid (white to black), lactose (white to black), creatine (white to black) and azo dicarbonamide (yellow to black) have been found most useful at their respective temperatures. Others which are found likely to be advantageous for particular end uses are D(+)-galactose, sucrose, methylene blue, β -alanine, methyl violet, glycine, nicotinic acid-N-oxide and 5-aminosalicylic acid.

It will be appreciated that many variations and modifications are possible within the basic concept of the present invention. For example the thermochromic ingredient before application to the heat-recoverable article may be part of an aqueous or non-aqueous vehicle comprising, for example, a polymeric binder, or may be part of a solid formulation, for example, a crayon based on a wax such as a paraffin wax. The nature of the thermochromic formulation will, of course, depend on the end use in a specific application.

Table

	Preferred	T _m (decomposition)	
15			15
		60—70	
	X	93	
		102—103°C	
20	X	103—105°C	20
	X	111	
		120	
		124—127	
	X	130	
25		132	25
	X	133	
		135	
	X	146	
		150	
30	X	165	30
	X	170	
	X	171—174	
	X	170	
		182—184	
35	X	185	35
	X	190—192	
	X	190—194	
	X	190	
	X	192—195	
40		196—197	40
	X	198	
		199—200	
		200—204	
	X	200	
45	X	205	45
	X	208—210	
		210	
		214—216	
		215	
50	X	215	50
	X	219	
		220	
		225	
		228—230	
55	X	234	55
		240	
		242	
		242—244	
	X	245	
60	X	250	60
		250—255	
		250—252	
		260	

	Phenyl-2-piperidyl-acetic acid		260—265	
	Succinamide		263—266	
	DL-phenylalanine	X	271—273	
5	5-amino-salicylic acid		280	5
	DL-methionine	X	281	
	DL-alanine	X	290	
	N-hydroxy ethylenediamine triacetic acid trisodium salt dihydrate		288—290	
10	Creatine	X	295	10
	2-amino octanic acid		295	
	Maleic acid dihydrazide	X	300	
	Nile blue	X	305	
	2-hydroxy-benzimidazole		318	
15	1,4-benzenedicarboxylic acid	X	325	15
	Dinicotinic acid	X	325	
	4,4-azobenzenedicarboxylic acid	X	330	
	6-uracilcarboxylic acid	X	347	
	Melamine	X	354	
20	Guanine	X	360	20
	Oxamide	X	400	

However, as will be understood from the foregoing discussion, the composition of the present invention is especially useful in the thermochromic marking of heat-recoverable articles, especially heat-shrinkable tubing, wrap-around sleeves and end-caps. For this purpose, it is advantageous to formulate a coating composition usually comprising a polymeric binder. 25

For example, one currently preferred temperature-indicating composition for the production of heat-recoverable articles according to the invention comprises the organic thermochromic material, e.g. allantoin, a polymeric binder, e.g. an acrylic resin, and an organic solvent, preferably a halogenated, e.g. chlorinated solvent. Chlorinated solvents have been especially useful because they are good solvents for the binder, have low toxicity, are non-flammable and evaporate quickly at room temperature because of their high vapour pressures. Amongst suitable chlorinated solvents there may be mentioned 1,1,1-trichloroethylene and mixtures thereof. 30

Suitable binder resins include acrylic resins such as those marketed under the Trade Mark Paraloid B-66 (Rohm & Haas) which is a copolymer of n-butylmethacrylate with methylmethacrylate. Other suitable materials include ethylene/vinyl acetate copolymers, ethylene/alkylacrylate copolymers, chlorinated polyethylenes, vinyl chloride homo- and co-polymers, especially vinylacetate/vinyl chloride co-polymers which may be wholly or partially hydrolyzed, and polyvinyl acetate, which may also be partially hydrolyzed. 35

However, it must be emphasized that other materials will be suited to different applications, including, for example, water-based latex paints. 40

Equally, the amount of thermochromic material incorporated may vary according to the application but in the coating compositions described above, will typically be in the range from 1 to 20%, especially from 5 to 10%, based on the weight of the composition.

Other ingredients can be added as appropriate. For example a pigment such as an organic dye, e.g. sunfast blue or sumatra yellow may be added for colouring purposes. Thickening agents, e.g. fumed silica (e.g. Cab-O-Sil and Aerosol) may be added to improve the rheological properties. In this respect, organic thickening agents with low melting points are especially preferred because they do not interfere with the colour change. 45

One such organic thickening agent is Thixatrol ST which is a derivative of castor oil sold by National Lead which may be used at levels of 0.5% by weight and higher, especially 1% and more, in the above described formulations. 50

Antioxidants, such as those marketed under the Trade Marks Irganox 1010 and Platinox 112, and plasticizers such as dioctyl phthalate may also advantageously be incorporated.

It is usually preferred to use a temperature-indicating composition according to the present invention which is initially green in colour, and this may be achieved by addition of suitable dye-stuffs to the formulation. A colour change to black or near-black is often desirable for optimum appearance when black heat-recoverable articles are installed, and this is readily achieved by the use of the aforementioned materials which decompose at the relevant temperature to give black or near-black decomposition products. 55

Mixtures of the decomposable materials may be used to produce a more gradual colour change as a signal to the operator that the desired temperature is being approached, and in such cases it is preferred to use 8.5 to 9.5 (especially about 9) parts of a material having a higher decomposition temperature to 0.5 to 1.5 parts (especially one part) of material(s) having a lower decomposition temperature. For example nine parts of allantoin to one part of ascorbic acid or sucrose could be used. 60

In some cases it has been found that the decomposition products may be leached out by long term exposure to moisture leaving behind a shell of binder which may incorporate enough dyestuff to resemble the original (unheated) colour of the chromogenic paint, thus leading to confusion as to whether or not the heat-recoverable product was correctly heated on installation. This effect can be rendered less troublesome by including in the formulation a background-colouring dyestuff which is itself decomposed during the heating. Methylene Blue is one possible material for this purpose but it is preferred to use the less water-soluble dyestuff Indigo Blue. A most preferred approach, however, is to attach the dyestuff or pigment to the decomposable material (e.g. allantoin) preferably by chemical coupling and preferably before it is incorporated in the temperature-indicating composition. The coupling bond may be ionic or covalent, and suitable bonds may be obtained by the use of appropriate coupling agents, for example sulphonyl or cyanuric chloride.

The thermochromic composition of the present invention is especially useful on heat-recoverable articles which are to be applied around a body, e.g. a cable splice, and have on their interior surface installed a coating which must be melted to ensure adequate sealing of the resulting enclosure. The composition in such cases is formulated to produce the colour change when the exterior surface of the article has been heated to a temperature which results in the desired melting of the interior coating when in contact with the substrate (assuming no abnormal heat-sink effects).

The following Example illustrates a typical thermochromic paint formulation for use in accordance with the present invention with heat-recoverable articles.

Compound	Parts by weight
Paraloid B-66 (Acrylic resin)	4.00
1,1,1-Trichloroethane	57.69
Perchloroethylene	20.00
Allantoin	16.00
Sunfast Blue or Cinquasia Green	0.06
Irganox 1010	0.25
Plastinox 1212	0.25
Diocetyl phthalate	0.50
Methanol/H ₂ O (smoothing agent)	0.25
Thixatrol ST	1.00

The present invention allows one to monitor and control heating of plastics articles, especially cross-linked polymeric articles such as the heat-recoverable products mentioned above, as well as other substrates and applications, including, for example, heat-recoverable articles made from memory metals as described in British Patents Nos. 1,327,441 and 1,488,393, especially the preconditioned alloys described and claimed in U.S. Patents Nos. 4,036,669; 4,067,752 and 4,095,999.

In contrast with the previously proposed inorganic thermochromic formulations which have sometimes been adversely affected by heat-aging, or environmentally undesirable, and have had an undesirable tendency to reverse colour, especially under wet or moist conditions and a tendency to deteriorate catalysed by acids and bases with a resultant change in temperature response, the organic compounds of the present invention are generally stable, non-reversible, environmentally acceptable, and give reproducible results.

A further preferred embodiment of the invention is that in which the melting/decomposition temperature is within the range 350—450°C, most preferably using oxamide (melting point 400°C) as the decomposable organic material. It has very surprisingly been found that this large increase (compared with allantoin) in colour change temperature on the outside of a heat-shrinkable sleeve results in only about 10°C increase in the bond-line temperature within the sleeve, and only about 10% increase in sleeve installation time. The oxamide composition may be especially useful in countering the effects of low-temperature installation environments.

Claims

1. A heat-recoverable article which is to be heated to a pre-selected temperature during installation or use, which is capable of forming an enclosure about a body, which carries on a surface which will face the interior of the enclosure a meltable composition, and which carries a temperature indicating composition on a surface which will be visible when the article is enclosing the body, the temperature indicating composition comprising decomposable organic material which, on heating of the article to the pre-selected temperature melts and decomposes substantially irreversibly to provide a visible colour change, said pre-selected temperature being a temperature which results in the melting of said meltable composition to effect sealing of the enclosure.
2. An article according to Claim 1, wherein the temperature indicating composition comprises a mixture of decomposable organic materials which melt and decompose at different temperatures from one another.

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3. An article according to Claim 2, wherein the temperature indicating composition comprises 8.5 to 9.5 parts by weight of a decomposable organic material having a higher decomposition temperature, and 0.5 to 1.5 parts by weight of a decomposable organic material having a lower decomposition temperature.

5 4. An article according to any one of Claims 1, 2 or 3, wherein the said decomposable organic material comprises allantoin. 5

5. An article according to any one of Claims 1, 2, or 3, wherein the said decomposable organic material comprises ascorbic acid, lactose, creatine or azo dicarbonamide.

10 6. An article according to any one of Claims 1, 2 or 3, wherein the said decomposable material comprises D(+)-galactose, sucrose, methylene blue, β -alanin, methyl violet, lysine, nicotinic acid-N-oxide, or 5-amino-salicylic acid. 10

7. An article according to Claim 1, wherein the temperature indicating composition is coloured by means of a pigment or dyestuff in addition to the said decomposable organic material.

15 8. A method of enclosing a body comprising selecting a heat-recoverable article which is capable of forming an enclosure about a body, which carries on a surface which will face the interior of the enclosure a meltable composition, and which carries a temperature indicating composition on a surface which will be visible when the article is enclosing the body, the temperature indicating composition comprising decomposable organic material which, on heating of the article to a pre-selected temperature, melts and decomposes substantially irreversibly to provide a visible colour change; positioning around the body the heat-recoverable article; and heating the article to at least the pre-selected temperature so as to (i) recover the article about said body, (ii) melt the meltable material to effect sealing of the enclosure, and (iii) to cause the temperature indicating composition to melt and decompose substantially irreversibly to undergo the visible colour change, the temperature indicating composition being visible. 20

25 9. A kit-of-parts for use in providing a sleeve enclosure around an elongate body; the kit including an article according to any one of Claims 1, 2, 3 or 7. 25

30 10. A kit-of-parts which comprises: a heat recoverable article for providing an enclosure about a body and which carries on a surface which will face the interior of the enclosure a meltable composition; and a coating composition for the heat recoverable article the coating composition comprising a polymeric binder resin and a thermochromic ingredient comprising a decomposable organic material; on heating the composition to a temperature between 80° and 400°C., the organic material melts and decomposes to provide a substantially irreversible visible colour change, thereby indicating melting of the meltable composition. 30

35 11. A kit-of-parts which comprises: a heat recoverable article for providing an enclosure about a body and which carries on a surface which will face the interior of the enclosure a meltable composition; and a solid composition in the form of a crayon, the crayon comprising a wax and a thermochromic ingredient comprising a decomposable organic material; on heating the composition to a temperature between 80° and 400°C., the organic material melts and decomposes to provide a substantially irreversible visible colour change, thereby indicating melting of the meltable composition. 35

40 12. A kit-of-parts which comprises: a heat recoverable article for providing an enclosure about a body and which carries on a surface which will face the interior of the enclosure a meltable composition; and a water based latex paint composition, the composition having a thermochromic ingredient comprising a decomposable organic material; on heating the composition to a temperature between 80° and 400°C., the organic material melts and decomposes to provide a visible colour change, thereby indicating melting of the meltable composition. 40

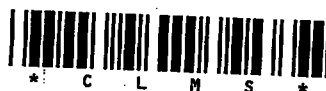
45 13. A method according to Claim 8, wherein the temperature indicating composition comprises a mixture of decomposable organic materials which melt and decompose at different temperatures from one another. 45

50 14. A method according to Claim 13, wherein the temperature indicating composition comprises 8.5 to 9.5 parts by weight of a decomposable organic material having a higher decomposition temperature, and 0.5 to 1.5 parts by weight of a decomposable organic material having a lower decomposition temperature. 50

15. A method according to any one of Claims 8, 13 or 14, wherein the decomposable organic material comprises allantoin.

55 16. A method according to any one of Claims 8, 13 or 14, wherein the decomposable organic material comprises a material selected from the group consisting of ascorbic acid, lactose, creatine or azo dicarbonamide. 55

60 17. A method according to any one of Claims 8, 13 or 14, wherein the decomposable material comprises a material selected from the group consisting of D(+)-galactose, sucrose, methylene blue, β -alanin, methyl violet, lysine, nicotinic acid-N-oxide, and 5-amino-salicylic acid. 60



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In some cases it has been found that the decomposition products may be leached out by long term exposure to moisture leaving behind a shell of binder which may incorporate enough dyestuff to resemble the original (unheated) colour of the chromogenic paint, thus leading to confusion as to whether or not the heat-recoverable product was correctly heated on installation. This effect can be rendered less troublesome by including in the formulation a background-colouring dyestuff which is itself decomposed during the heating. Methylene Blue is one possible material for this purpose but it is preferred to use the less water-soluble dyestuff Indigo Blue. A most preferred approach, however, is to attach the dyestuff or pigment to the decomposable material (e.g. allantoin) preferably by chemical coupling and preferably before it is incorporated in the temperature-indicating composition. The coupling bond may be ionic or covalent, and suitable bonds may be obtained by the use of appropriate coupling agents, for example sulphonyl or cyanuric chloride.

The thermochromic composition of the present invention is especially useful on heat-recoverable articles which are to be applied around a body, e.g. a cable splice, and have on their interior surface installed a coating which must be melted to ensure adequate sealing of the resulting enclosure. The composition in such cases is formulated to produce the colour change when the exterior surface of the article has been heated to a temperature which results in the desired melting of the interior coating when in contact with the substrate (assuming no abnormal heat-sink effects).

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A further preferred embodiment of the invention is that in which the melting/decomposition temperature is within the range 350—450°C, most preferably using oxamide (melting point 400°C) as the decomposable organic material. It has very surprisingly been found that this large increase (compared with allantoin) in colour change temperature on the outside of a heat-shrinkable sleeve results in only about 10°C increase in the bond-line temperature within the sleeve, and only about 10% increase in sleeve installation time. The oxamide composition may be especially useful in countering the effects of low-temperature installation environments.

Claims

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2. An article according to Claim 1, wherein the temperature indicating composition comprises a mixture of decomposable organic materials which melt and decompose at different temperatures from one another.



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18. A method according to Claim 8, wherein the temperature indicating composition is coloured by means of a pigment or dyestuff in addition to the decomposable organic material.

19. An article according to Claim 1, wherein the temperature indicating composition is substantially as herein described with reference to the foregoing example.

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