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(54) **Title:** THERMOCHROMIC COATINGS WITH RESIN VEHICLE

(57) **Abstract:** Thermo-chromic coatings are improved by mixing thermo-chromic capsules with polymer resins in a manner that imparts shelf stability to flowable precursors that may be cured to form relatively hard coatings that are capable of withstanding machine operations, such as the operations needed to make beverage can lids, bottle caps, pull tabs and the like.

## THERMOCHROMIC COATINGS WITH RESIN VEHICLE

## RELATED APPLICATIONS

[0001] This application claims benefit of priority to provisional application serial no. 61/443,170 filed February 15, 2011.

## BACKGROUND

[0002] Thermochromic encapsulated dyes undergo a color change over a specific temperature range. By way of example, a dye may change from a particular color at low temperature to colorless at a high temperature, such as red at 85°F and colorless at above 90°F. The color change temperature is controllable, such that the color-change can take place at different temperatures. In one example, the color change may occur at a temperature just below a person's external body temperature so that a color change occurs in response to a human touch. For those skilled in the art of thermochromic microcapsule synthesis, the precise control of the temperatures at which color changes occur is easily achievable. For example, the ideal temperature of color change for cool beverages may range from 0°C to 15°C, while the ideal temperature change for a warm or hot beverage may lie between 40°C and 65°C.

[0003] Thermochromic systems consist of three main components: an electron donating chromophore, an electron-accepting color developer and a non-polar solvent that facilitates color change over a specified temperature range. The properties of thermochromic systems have been exploited for more than 35 years. One technique used to produce the thermochromic encapsulated dye is to combine water, dye, developer, oil, with urea-formaldehyde or melamine-formaldehyde resin and agitate to create a very fine emulsification. Interfacial tensions are such that the oil, dye and developer end up on the inside of a urea-formaldehyde or melamine-formaldehyde capsule distributed primarily throughout the water phase. The urea-formaldehyde or melamine-formaldehyde substance, while very hard and resistant to breakdown at high temperature, is permeable. Though there has been significant improvement in microencapsulation technology, thermochromic systems still have inherent chemical instability in polar solvent-based systems. For this reason, microencapsulated thermochromic pigments have found limited applicability in solvent-based

systems. For example United States Patent No. 6,139,779 describes how low molecular weight solvents (generally less than 100 g/mol) have been shown to permeate the relatively thin microcapsule wall and destroy the thermochromic system. A variety of thermochromic inks may be purchased on commercial order, for example, from Chromatic Technologies, Inc. of Colorado Springs, Colorado.

**[0004]** United States Patents 4,421,560 and 4,425,161 entitled "Thermochromic Materials" both state that thermochromic inks can be made with "conventional additives used to improve conventional printing inks." Nonetheless, there are concerns over what additives may be added to these inks.

**[0005]** Thermochromic dye is often sold in a slurry of pigment formed of encapsulated dye in a water base. It happens that the pH of this slurry is most often neutral in a range from 6.5 to 7.5. When thermochromic dye is added to a formulation that has a pH outside this range, the color change properties are often lost. This can be an irreversible effect and, therefore, it is important to adjust the pH prior to adding the thermochromic dye.

**[0006]** Several types of ingredients are traditionally added to ink formulations. The combination of all the ingredients in an ink, other than the pigment, is called the vehicle. The vehicle carries the pigment to the substrate and binds the pigment to the substrate. The correct combination of vehicle ingredients will result in the wetting of a pigment. This wetting means that the vehicle forms an absorbed film around the pigment particles. The main ingredient in an ink is the binder. This may be a resin, lacquer or varnish or some other polymer. The binder characteristics vary depending on the type of printing that is being done and the desired final product. The second main ingredient is the colorant itself, for example, as described above. The remaining ingredients are added to enhance the color and printing characteristics of the binder and the colorant. These remaining ingredients may include reducers (solvents), waxes, surfactant, thickeners, driers, and/or UV inhibitors.

**[0007]** Plain lids of the type used in beverage cans are stamped from a coil of aluminum, typically alloy 5182-H48, and transferred to another press that converts the stamped materials into easy-open ends. The conversion press forms an integral rivet button in the lid and scores the opening, while concurrently forming the tabs in another die from a separate strip of aluminum. The tab is pushed over the button, which is then flattened to form the rivet that attaches the tab to the lid. The top rim of the can is trimmed and pressed inward or "necked" to form a taper conical where the can will later be filled and the lid (usually made of an aluminum alloy with magnesium) attached. The lid components, especially the tabs,

may be coated before they are subjected to such manufacturing processes as riveting. can ends, tabs, caps or closures.

**[0008]** Three piece beverage cans are usually filled before the top is crimped in place. The filling and sealing operations are fast and precise. The filling head centers over the can and discharges the beverage to flow down the sides of the can. The lid is placed on the can then crimped in two operations. A seaming head engages the lid from above while a seaming roller to the side curls the edge of the lid around the edge of the can body. The head and roller spin the can in a complete circle to seal all the way around. A pressure roller next drives the two edges together under pressure to make a gas-tight seal. Filled cans usually have pressurized gas inside, which stiffens the filled cans for subsequent handling.

**[0009]** Thermochromic inks have been used successfully as indicators of a preferred usage temperature and as a brand differentiator. Specifically, thermochromic inks have been used as cold indicators on aluminum cans, via metal decorating inks, to communicate optimum consumption temperature to the consumer. This interactivity through thermochromic color change so far does not extend to coating on can ends, tabs, caps and closures. To date, no such coatings are commercially available. In part, this is due to significant mechanical forces that are applied to precoated coil stock to form can ends, tabs, caps and other closures. Because of the stress and sheer during the tooling process the coating must be flexible and resistant to cracking, flaking, and other damage. In addition, the coating must be sufficiently chemically resistant to be unaffected by pasteurization or other processes. In order to meet the above requirements, the reversible thermochromic coating described herein must contain a thermochromic pigment, a formulated vehicle system and/or a commercially-available coating commonly used for can and coil coatings. In order to engineer additional coating properties, for example, chemical resistance or flexibility, components such as a curing agent, an accelerator or catalyst to enhance curing, or wax may be added. Furthermore, thermochromic microcapsule wetting agents may be incorporated to aid pigment dispersion, and one or more solvents may be selected. United States patent application 2003/0127415 A1 describes the use of thermochromic inks to apply printable images to metal lids and caps. United States Patent Application 2011/0226636 A1 describes the use of thermochromic inks as applied in multiple ways to aluminum can ends, the displaceable tear panel and the non-detachable tab. While these disclosures describe the application of thermochromic inks, they do not teach practical means of achieving the claims described. Conventional thermochromic inks are generally unsuited for the manufacturing stresses involved in making the can ends and tabs which, practically speaking, are made from

aluminum rolls commonly known as coil stock that must be coated prior to the machining operations that form the can ends, tabs, caps and other closures. Because of the durability and chemical stability of epoxy coatings, these are commonly applied to aluminum and metal cans where direct or indirect food contact may occur. The prior art does not, however, provide detailed formulations for a reversible thermochromic epoxy-based, or other resin systems, for use in can ends, tabs, caps or closures.

[0010] It is problematic that existing thermochromic coatings fail to withstand the stresses of these manufacturing operations which may, for example, excessively thin or scratch the coatings or crush the microcapsules forming the thermochromic pigment.

#### SUMMARY

[0011] The presently disclosed instrumentalities overcome the problems outlined above and advance the art by providing reversible thermochromic can and coil coatings to fabricate can ends, tabs, caps and/or closures using aluminum or steel alloys. Furthermore, the inventors have discovered processes in the manufacture of the thermochromic microcapsule as well as processing conditions when making the coating that enhance the solvent stability of the thermochromic pigment.

[0012] The use of thermochromic systems as a substitute for conventional pigments in resin based coatings creates an interactive effect which can provide an indicator or purely artistic effect. In addition to the visual appeal of thermochromic can ends, tabs, caps and closures, they have also a functional purpose indicating the internal temperature of the beverage within the can as, for example, the pigment changes from colorless to colored or from one color to a different color.

[0013] In one aspect, a thermochromic coating may include a pigment and a vehicle. The pigment is present in an amount ranging from 1% to 40% of the coating by weight, and the vehicle forms the balance of from 99% to 60% by weight. The pigment may be provided in a slurry form having various liquid content, so for consistency the weight of pigment is assessed using pigment that is completely dry. For example, pigment that is provided in a water-based slurry would be assessed after elimination of the water, although it is not strictly necessary to eliminate the water when mixing all formulations.

[0014] The pigment includes thermochromic microcapsules. These are usually urea-formaldehyde or melamine-formaldehyde resins encapsulating a core that contains a thermochromic system including a thermochromic dye (such as a leuco dye), a developer and a solvent that controls the color activation temperature of the dye and developer. Other

thermochromic systems are known to the art. Methods of forming thermochromic capsules with predetermined activation temperatures are well known in the art. The pigment may also contain dyes or solids that impart color and are not thermochromic in nature.

[0015] The vehicle contains a polymerizable resin that contains the pigment and may be, for example, epoxy, polyester, urethane, acrylic acid and acrylate. These may incorporate curing agents as are known in the art, such as primary, secondary, tertiary, and cyclic aliphatic amines, blocked amines (e.g. Hycat), amino resins with a range of alkylation, aromatic amines, polyamines, polyamides, amidoamines, ketimines, melamine resins, isocyanates or resins that can be cured using ultraviolet radiation. Surfactants or other dispersing agents may facilitate dispersion of the pigment in the vehicle. The dispersing agents may suitably include, for example, nonionic, anionic, cationic, or zwitterionic surfactants, polymers or copolymers, or reactive diluents such as aliphatic or cycloaliphatic glycidyl ethers. Nonpolar alkane or aromatic solvents, polar, aprotic solvents such as esters, ketones, amides or polar, protic solvents such as alcohols or acids may be added for rheological control.

[0016] In one embodiment, a thermochromic coating formulation includes:

<b>Ingredient</b>	<b>Weight Percent of Coating</b>
<b>Pigment*</b>	1% to 40%
<b>Vehicle</b>	
Polymerizable resin	5% to 30%
Dispersing agent	0% to 5%
Solvent	0% to 50%
Curing agent	0% to 25%
Wax	0% to 5%

\*Assessed by solids content upon complete drying of pigment capsules, but does not need to be dried and may be mixed as a slurry.

[0017] In one aspect, a reversible thermochromic coating for use in can and coil coatings contains a reversible thermochromic pigment in an amount from 1% to 40% by

weight of the coating, and a vehicle forming the balance of the coating. The vehicle includes a resin selected from the group consisting of epoxy, polyester, urethane, acrylic acid and acrylate resins, and combinations thereof. Commercially available thermochromic pigments may be readily obtained in a variety of colors demonstrating color transition temperatures from about 5 °C and up to about 65 °C. A range of color formulations may be made by mixing the pigment to include one or more of the following reversible thermochromic colors: yellow, magenta, cyan, and black. These may be further mixed to include other dyes or solid pigments that are non-thermochromic in nature. The pigment may change from a colorless state to a colored state upon cooling to the reactive temperature, or to a colored state upon heating to the reactive temperature. It is preferred that the microcapsules are formed of urea-formaldehyde or melamine-formaldehyde that is acid catalyzed to enhance the inherent stability in polar, low molecular weight solvents having a molecular weight of about less than 100 g/mol.

[0018] When premixed using a nonpolar solvent, the coatings can demonstrate shelf stability exceeding 14 or 45 days when stored at about 20°C. Some coating formulations demonstrate shelf stability in excess of one year.

[0019] The curing agent is generally compatible with the resin for this purpose and may be, for example, a latent blocked amine to initiate a polymerization reaction upon heating.

[0020] The coating is preferably roller-coated onto coil stock aluminum or steel and the roll stock aluminum is subsequently formed into one or more beverage can components. These components may be selected from the group consisting of beverage can ends, beverage can tabs, bottle caps, and/or beverage container closures. The aluminum is preferably an alloy that is commonly used in canning operations, such as aluminum alloy 5182-H48. The coating process preferably occurs in one or more coats to yield a dried film with a thickness ranging from 1 mg/in<sup>2</sup> up to 5.5 mg/in<sup>2</sup>.

#### BRIEF DESCRIPTION OF THE FIGURES

[0021] Figure 1 compares beverage cans with ends that are coated with a thermochromic coating according to the present disclosure and chilled to different temperatures corresponding to Fig. 1A and Fig. 1B.

[0022] Fig. 2 shows a beverage can lid having a pull tab with a thermochromic coating.

[0023] Fig. 3 shows a process of applying the coating to make thermochromically functional aluminum that can be used to fabricate thermochromically functional beverage can components.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0024] Thermochromic ink coatings contain, in combination, a vehicle and a pigment including thermochromic microcapsules. The thermochromic microcapsules are preferably present in an amount ranging from 1% to 50% of the coating by weight on a sliding scale. The vehicle contains a solvent that is preferably present in an amount ranging from 25% to 75% by weight of the coating.

##### **Pigment**

[0025] Careful preparation of encapsulated reversible thermochromic material enhances coating stability in the presence of low molecular weight polar solvents that are known to adversely affect thermochromic behavior. One skilled in the art of microencapsulation can utilize well-known processes to enhance the stability of the microcapsule. For example, it is understood that increasing the cross linking density will reduce the permeability of the capsule wall, and so also reduces the deleterious effects of low molecular weight polar solvents. It is also commonly understood that, under certain conditions, weak acids with a  $pK_a$  greater than about 2 may catalyze microcapsule wall polymerization and increase the resulting cross linking density. It is presently the case that using formic acid as a catalyst enhances solvent stability of blue thermochromic microcapsules in the presence of low molecular weight ketones, diols, and aldehydes at room temperature. Further, it is well understood that increasing the diameter of the thermochromic microcapsule can result in enhanced solvent stability.

[0026] The selection of material for use as the nonpolar solvent for the thermochromic dye and color developer that is encapsulated within the thermochromic pigment determines the temperature at which color change is observed. For example, changing the solvent from a single component to a two-component solvent system can shift the temperature at which full color is perceived almost  $7^\circ\text{C}$  from just under  $19^\circ\text{C}$  to  $12^\circ\text{C}$ . The present disclosure shows how to apply this knowledge in preparing resin-based vehicle coatings for use in can and coil coatings with full color temperatures, i.e., the temperature at which maximum color intensity is observed, as low as  $-5^\circ\text{C}$  and as high as  $65^\circ\text{C}$ . No adverse effects on the physical properties of the resulting coating were observed as the full color



temperature was changed over the above temperature range by the use of different straight chain alkyl esters, alcohols, ketones or amides.

[0027] Thermochromic materials including encapsulated thermochromic systems with a variety of color properties may be purchased on commercial order from such companies as Chromatic Technologies, Inc., of Colorado Springs, Colorado.

[0028] Control over observed color intensity is demonstrated in several ways, generally by presenting providing increased amounts of pigment. For a typical coating, material thickness ranges from 1 mg/in<sup>2</sup> to 6 mg/in<sup>2</sup>. Very intense color is observed for coatings with thickness greater than about 3 mg/in<sup>2</sup>. Increasing thermochromic pigment solids can also result in a more intense observed color even when coating thickness is decreased. However, dried film properties such as flexibility and toughness may be compromised if too much thermochromic pigment is incorporated. The optimal range of thermochromic pigment solids is within 5 to 40% by weight of the coating.

### **Vehicle**

[0029] Physical properties of the finished coating can be significantly affected by the selection of resin to be used. When no resin is used in formulating a reversible thermochromic coating, a matte finish is achieved that is able to be formed into can ends, tabs, caps and/or other closures. While this result may be desired, the inclusion of a low viscosity, relatively low molecular weight resin, monomer, oligomer, polymer, or combination thereof, can enhance gloss and affect other physical film properties such as hardness, flexibility and chemical resistance. The resin is designed to supplement the total solids deposited on the substrate, thus impacting the physical properties of the dried film. Any resin material, monomer, oligomer, polymer, or combination thereof, that can be polymerized into the commercially-available can and coil coating material is suitable for inclusion in the formulation of the current reversible thermochromic can and coil coating. Acceptable classes of resins include, but are not limited to, epoxy, polyester, urethane, acrylic acid and acrylate, or other types of resin systems with suitably high solids content.

[0030] Final coating properties such as chemical resistance, hardness and flexibility can be manipulated by selection of cross linkers or curing agents. Materials that readily react with and incorporate into the selected resin system is suitable for inclusion as a cross linker or curing agent. Examples include, but are not limited to, primary, secondary, tertiary, and cyclic aliphatic amines, blocked amines, amino resins with a range of alkylation, aromatic amines, polyamines, polyamides, amidoamines, ketimines, melamine resins,

isocyanates or resins that can be cured using ultraviolet radiation. Care should be taken to balance reactivity needs with pot life / shelf life. For example, if the curing agent reacts too quickly with the resin, the reversible thermochromic coating may cure before the coating can be applied to the aluminum or steel substrate.

**[0031]** In order to ensure the reversible thermochromic coating fully cures before the coil is re-wound, accelerators and/or catalysts may be added to the coating formulation. Examples of suitable materials for use as cure accelerators or catalysts include, but are not limited to, imidazoles, amidoamines, linear phenolics, blocked and unblocked acid catalysts, isocyanates, dihydrazides or photoinitiators.

**[0032]** Coating properties can also be manipulated with the inclusion of natural or synthetic waxes. For example, carnuba, polytetrafluoroethylene (PTFE), or a combination thereof may be included to affect physical film properties such as slip, coefficient of friction and abrasion resistance.

**[0033]** Adequate dispersion of thermochromic pigment throughout the resin is an aspect of achieving high quality coatings for commercial use. The inclusion of additional molecular or polymeric dispersing aids, such as nonionic, anionic, cationic or zwitterionic surfactants, polymers or copolymers, can ensure adequate dispersion. Active diluents, in addition to reacting with the resin selected, may also function as a dispersing aid. Furthermore, active diluents can reduce the coating viscosity and affect film flexibility and impact resistance. Suitable materials to be included as an active diluent include, but are not limited to, aliphatic or cycloaliphatic glycidyl ethers, monofunctional and polyfunctional glycidyl ethers.

**[0034]** Final adjustments to coating rheology may be made by the addition of select reducers, or solvents. A reversible thermochromic coating can be adjusted to meet rheological criteria established for use in a roller coating application. Many solvents are available for this purpose. Care should be exercised to select solvents most compatible with thermochromic pigment systems. Nonpolar solvents or solvents of low polarity are preferred. However, modifications to thermochromic pigment preparation initiated by the inventors as well as the different coating preparations available to the inventors increased the solvent options available to include low molecular weight polar solvents such as esters, for example butyl carbitol acetate, low molecular weight alcohols such as ethanol or butanol, or ketones such as acetone.

**[0035]** The chemical stability and shelf life of the reversible thermochromic coating may be enhanced in various ways. In one aspect, this involves separating the

thermochromic pigment from organic solvents. A two-part coating system containing thermochromic pigment and resin in Part A and commercially-available coating material and other solvents in Part B is then mixed immediately prior to coating aluminum or steel alloys. The shelf life of the fully mixed coating material ranges from several days to many months depending on the identity of the other components selected.

[0036] For those situations for which a two-part solution is not preferable, stability can be balanced with convenience by preparing a one-part reversible thermochromic coating. In this case, careful selection of formulation components is paramount. The use of water-based commercially-available can and coil coating material enhances the shelf life stability by minimizing the amount of organic solvents in contact with the thermochromic pigment system. In one example, coating degradation was observed within 14 days when red thermochromic coatings were prepared using butyl carbitol acetate and stored at room temperature. Enhanced stability was observed when formulation components were modified as well as when stability enhanced thermochromic pigment systems were used.

[0037] The nonlimiting embodiments that follow teach by way of example and should not be construed as unduly limiting the scope of this disclosure.

#### **EXAMPLE 1—Two Part Coating**

Part A (30% by weight of coating)

Thermochromic pigment (any color)\*

Part B (70% by weight of coating)

Clear Coating (an epoxy coating available from Watson Standard of Pittsburgh, Pennsylvania)

\* This material may be purchased on commercial order from Chromatic Technologies, Inc. of Colorado Springs Colorado, and may include for example S5BOXX3105W, a blue thermochromic slurry that goes from a colored to colorless state when the temperature exceeds 31°C.

#### **EXAMPLE 2 – Two Part Coating**

Part A (60% by weight of coating)

45% Thermochromic Pigment (any color)\*

50% Epoxy resin (for example Epon 863 available from Lawter of LaVergne, Tennessee)

3.3% Dispersing aid (for example Disperbyk 2025 available from Byk of Wallingford, Connecticut)

1.7% Curing agent (for example Ancamine 2458 available from Air Products of Allentown, Pennsylvania)

Part B (40% by weight of coating)

85% Clear Coating (an epoxy coating available from Watson Standard of Pittsburgh, Pennsylvania)

15% Solvent to reduce viscosity (for example, butyl carbitol acetate available from Lawter of LaVergne, Tennessee)

\* This material may be purchased on commercial order from Chromatic Technologies, Inc. of Colorado Springs Colorado, and may include for example S5BOXX3105W, a blue thermochromic slurry that goes from a colored to colorless state when the temperature exceeds 31°C.

### **EXAMPLE 3 One Part Coating**

20% (w/w) Thermochromic Pigment (any color)\*

13% Polyester resin (for example, Decotherm 290 available from Lawter of LaVergne, Tennessee)

0.5% (w/w) Dispersing aid (for example, Byk 370 available from Byk of Wallingford, Connecticut)

7% (w/w) Curing agent 1 (for example, Cymel 328 available from Cytec Industries of Woodland Park, New Jersey)

1.5% (w/w) Curing agent 2 (for example, imidazole available from Aldrich of St. Louis, Missouri)

2% (w/w) Wax (for example, Fluoron 735 available from Lawter of LaVergne, Tennessee)

30% (w/w) Solvent (for example, ethyl-3-ethoxypropionate available from Univar of Redmond, Washington)

26% (w/w) Clear Coating (an epoxy coating available from Watson Standard of Pittsburgh, Pennsylvania)

#### **EXAMPLE 4 One Part Coating**

15% (w/w) Thermochromic Pigment (any color)\*

10% (w/w) Resin (for example, Epon 896 available from Lawter of LaVergne, Tennessee)

1.5% (w/w) Dispersing aid (for example, Disperbyk 112 available from Byk of Wallingford, Connecticut)

0.5% (w/w) Curing agent 1 (for example, Nacure 2500 available from King Industries of Norwalk, Connecticut)

4% (w/w) Curing agent 2 (for example, Cymel 325 available from Cytac Industries of Woodland Park, New Jersey)

1.5% (w/w) Wax – 0.5 wt % (for example, Ultrapoly 211A available from Lawter of LaVergne, Tennessee)

5% (w/w) Solvent 1 (for example, Heloxy Modifier 62 available from Lawter of LaVergne, Tennessee)

21.5% (w/w) solvent 2 (for example, ethyl-3-ethoxypropionate available from Univar of Redmond, Washington)

41% (w/w) Clear Coating (an epoxy coating available from Watson Standard of Pittsburgh, Pennsylvania)

**[0038]** Fig. 1 compares the lids of identical beverage cans 100 (Fig. 1A), and 150 (Fig. 1B). The cans 100, 150, differ in that can 100 is at room temperature and can 150 is chilled to a preferred temperature for human consumption of a beverage inside can 150. Lids 102, 152 are coated with epoxy-based thermochromic coatings 104, 154. The relative darkness of lid 152 compared to lid 102 indicates that a beverage (not shown) within can 150 is sufficiently chilled to a recommended temperature for improved palatability. As is known in the art, the lids 102, 152 contain tabs 106, 156 that may be pulled to open access to space within the interior walls of cans 100, 150, such that liquid or other matter may be poured into

or out of the cans through closures 108, 158 that are scored to rupture when the tabs 106, 156 are lifted.

**[0039]** As opposed to placing thermochromic ink on the entire lid, it is possible to coat selected elements of the can lid, such as the just the tab, just the closure, or both the lid and the tab without coating the closure. This is shown for example in Fig. 2 where can 200 has a tab 202 that is covered with a thermochromic coating as described above. The same coating or one having a different color and/or color transition temperature may be selectively applied to any feature of lid 201, such as surface 204, closure 206, an indented area 208 surrounding closure 206, and/or rim 210.

**[0040]** Fig. 2 shows a beverage can 200 with a pull tab 202 that has been covered with the coating of any of Examples 1 through 4. The tab 202 is manufactured from coil stock that is precoated with any of the coatings described above before the tab is formed.

**[0041]** Fig. 3 is a process diagram that shows sequential processing steps 300 for applying the thermochromic coating to coil stock of aluminum 302. As the sheet aluminum unwinds 303 from roll 302, a roller coater 304 receives an uncured thermochromic coating material 306, as described above. This places a liquid coating or film 308 on the aluminum. This film is cured, for example by the application of heat or ultraviolet radiation, at curing station 310, and the sheet 309 including the dried film 309 is coiled 311 onto roll 312. This roll 312 may then be used to make beverage can components as discussed in context of Figs. 1 and 2. It will be appreciated that additional coating operations (not shown) may be performed on sheet 309.

**[0042]** Those skilled in the art will appreciate that the various embodiments described herein teach by way of example and not by limitation. These embodiments may be subjected to insubstantial changes without departing from the true scope and spirit of the invention. Accordingly, the inventors hereby state their intention to rely upon the Doctrine of Equivalents in protecting their rights in what is claimed.

[0043]

CLAIMS

1. A reversible thermochromic coating for use in can and coil coatings, said reversible thermochromic coating comprising,  
a reversible thermochromic pigment in an amount from 1% to 50% by weight of the coating,  
and  
a vehicle forming the balance of the coating,  
the vehicle including a resin selected from the group consisting of epoxy, polyester, urethane, acrylic acid and acrylate resins, and combinations thereof.
2. The coating of claim 1 wherein the vehicle further comprises a wetting agent to facilitate dispersion of the pigment in the vehicle.
3. The coating of claim 1 wherein the vehicle further comprises a curing agent/accelerator to speed curing of the resin.
4. The coating of claim 1 wherein the vehicle further comprises a wax to improve surface properties of the coating when cured.
5. The coating of claim 1 wherein the vehicle further comprises a solvent affecting rheological properties of the coating.
6. The coating of claim 5 wherein the solvent is a polar solvent.
7. The coating of claim 6 wherein the coating is premixed and exhibits reversible thermochromic behavior for at least 14 days when stored at a temperature of about 20 °C.
8. The coating of claim 6 wherein the coating is premixed as a two part system and exhibits reversible thermochromic behavior for at least 45 days when stored at a temperature of about 20 °C.

9. The coating of claim 1, wherein said thermochromic pigment contains microcapsules formed with an acid catalyst effective to enhance the inherent stability in polar, low molecular weight solvents having a molecular weight of about less than 100 g/mol.
10. The coating of claim 1, wherein said thermochromic microcapsule achieves color change between a temperature of about -5 °C and up to about 65 °C.
11. The coating of claim 1, wherein said thermochromic coating is selected from the group of colors consisting essentially of a color selected by combining of one or more of the following reversible thermochromic colors: yellow, magenta, cyan, black.
12. The coating of claim 1, wherein a color change effect obtained by mixing thermochromic colors with conventional pigments or colored commercially-available can and coil coating material.
13. The coating of claim 1, wherein a change from a colored state to a different colored state upon cooling to the reactive temperature.
14. The coating of claim 1, wherein a change from a colorless state to a colored state upon cooling to the reactive temperature.
15. The coating of claim 1 containing 5 to 40 % by weight of thermochromic microcapsule solids.
16. The coating of claim 1 containing 5 to 30% by weight resin.
17. The coating of claim 1 containing 0 to 5% by weight of thermochromic microcapsule wetting agents.
18. The coating of claim 1 containing 0 to 25% by weight of a curing agent.
19. The coating of claim 1 containing 0 to 5% by weight of an accelerator and/or catalyst.



20. The coating of claim 5 containing 0 to 5% by weight of wax.
21. The coating of claim 5 containing 0 to 50% by weight of solvent(s).
22. The coating of claim 1 wherein said resin is curable at elevated temperatures or using an ultraviolet curing system.
23. A method of using the coating of claim 1, wherein the coating is applied by roller coating to roll stock metal and the roll stock aluminum is subsequently formed into one or more beverage can components selected from the group consisting of beverage can ends, beverage can tabs, bottle caps, and/or beverage container closures.
24. The method of claim 23 wherein the roll stock metal is a coiled sheet of aluminum.
25. The method of claim 23 wherein said reversible thermochromic coating of claim 1 wherein the beverage can component has a color activation temperature effective for use as an indicator of beverage temperature.
26. The method of claim 23 wherein the coating of claim 1 wherein said coating is applied in one or more coats to yield a dried film thickness ranging from 1 mg/in<sup>2</sup> up to 5.5 mg/in<sup>2</sup>, thereby controlling observed color intensity.
27. A three piece steel can having a component that is coated with the coating of claim 1.

FIG. 1

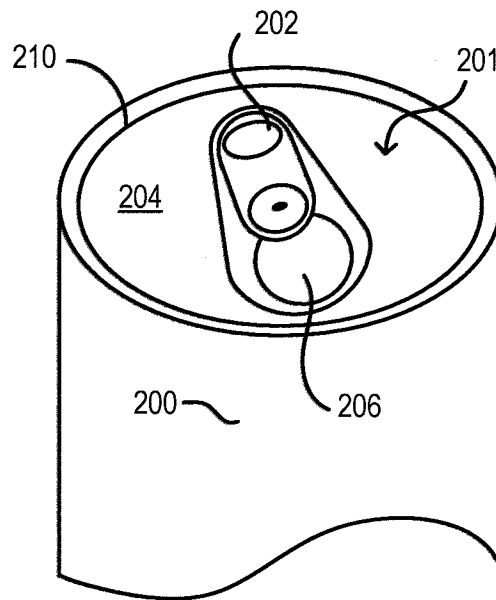
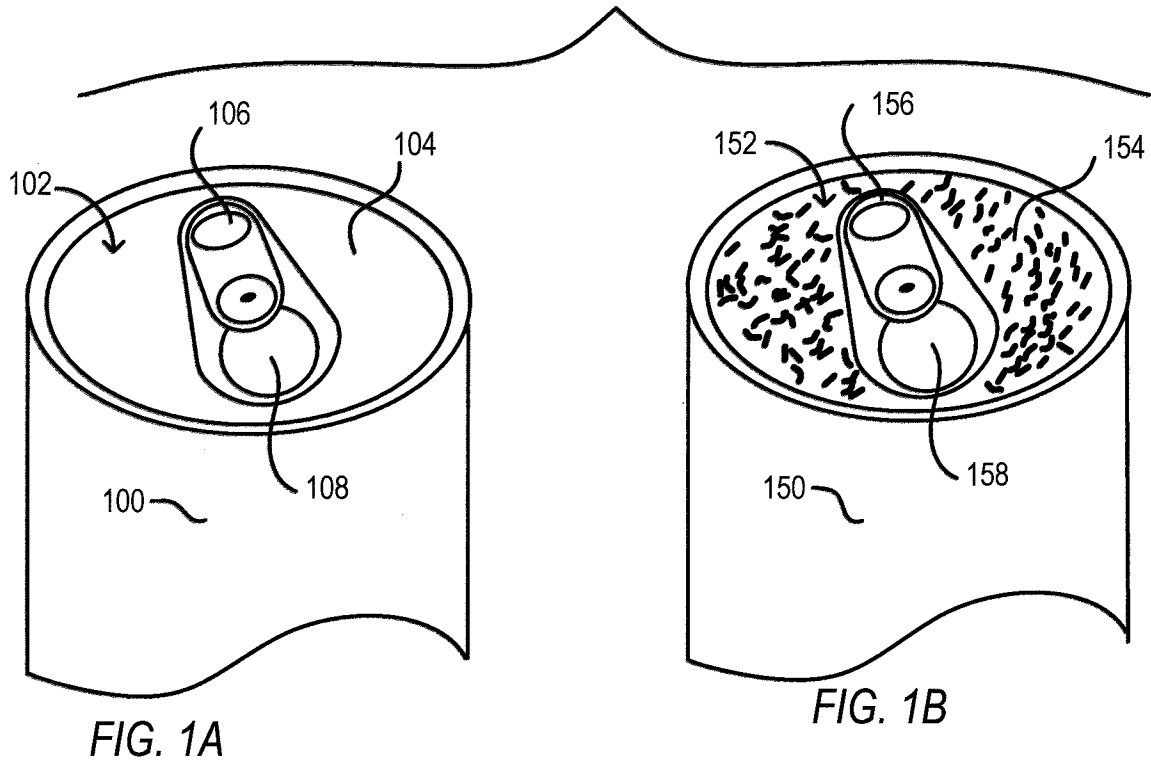


FIG. 2

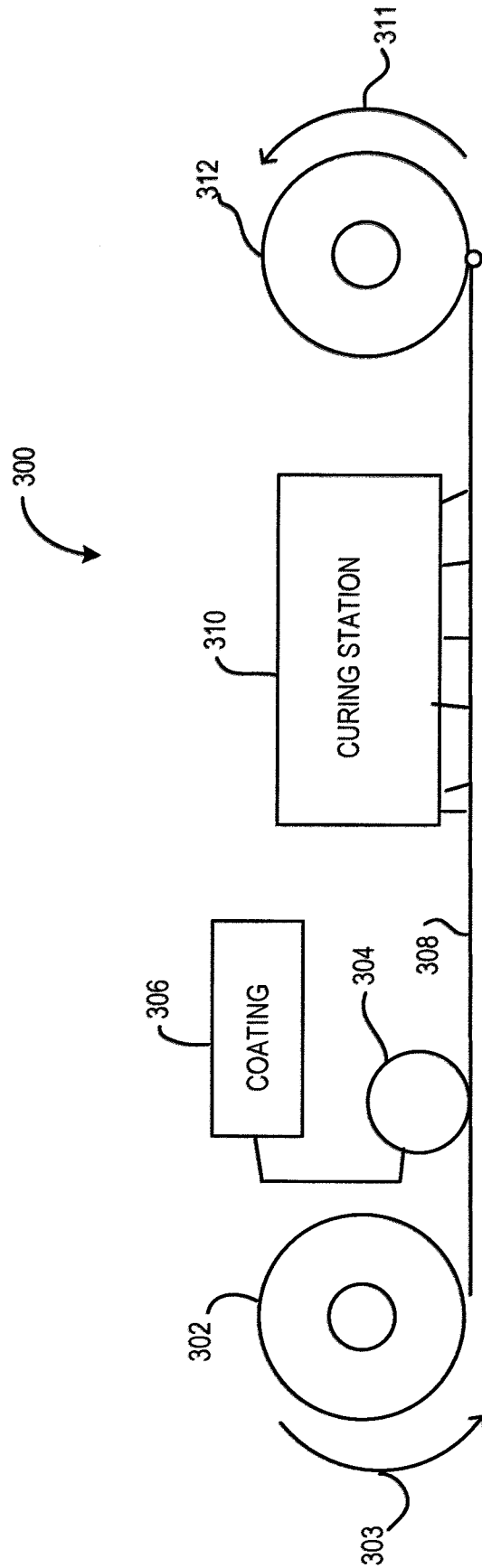


FIG. 3

**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/US2012/025322

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C09D5/00  
 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)  
 C09D

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/143516 A1 (MACDONALD JOHN GAVIN [US] ET AL) 4 June 2009 (2009-06-04) paragraph [0007] - paragraph [0011] claims 1,3-6,11,13,14,18,26,38,53; examples 1-3	1-27
X	WO 2007/120855 A2 (EBI LP [US]; HALANSKI MATTHEW A [US]; HEIBERG ERIC [US]; MCCORMICK STE) 25 October 2007 (2007-10-25) paragraph [0006] - paragraph [0009] paragraph [0028] - paragraph [0038] claims 1-4,7, 8,12,14,23; example 1 ----- -/--	1-27

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>
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Date of the actual completion of the international search  2 April 2012	Date of mailing of the international search report  12/04/2012
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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  Glomm, Bernhard
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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2012/025322

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/008774 A1 (YASUDA MICHIOYUKI [JP] ET AL) 9 January 2003 (2003-01-09) paragraph [0004] - paragraph [0005]; figures 1-4 claims 1,4; examples 1-9 -----	1-27
X	KR 920 010 717 B1 (KOLON INC [KR]) 14 December 1992 (1992-12-14) the whole document -----	1-27
X	EP 0 357 844 A1 (AKZO NV [NL]) 14 March 1990 (1990-03-14) page 2, line 24 - line 36 claims 1-3,8-11; examples 1,2 -----	1-27

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/US2012/025322
---

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009143516	A1	04-06-2009	EP 2215149 A2 11-08-2010
			US 2009143516 A1 04-06-2009
			WO 2009069059 A2 04-06-2009
-----			
WO 2007120855	A2	25-10-2007	NONE
-----			
US 2003008774	A1	09-01-2003	NONE
-----			
KR 920010717	B1	14-12-1992	
EP 0357844	A1	14-03-1990	AT 89306 T 15-05-1993
			CA 1336731 C 15-08-1995
			DE 3881046 T2 04-11-1993
			EP 0357844 A1 14-03-1990
			ES 2040832 T3 01-11-1993
			JP 2117971 A 02-05-1990
			US 5194183 A 16-03-1993
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