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(54) Heat sensitive record material.

(57) Heat sensitive record material in which microcapsules of a polyisocyanate/active hydrogen compound reaction product comprise a chromogenic-material; microcapsules as such.

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HEAT SENSITIVE RECORD MATERIAL

Field of the Invention

The invention relates to heat sensitive record material.

Statement of the Invention

The invention provides a heat sensitive record material comprising a support and a recording layer, said recording layer comprising microcapsules containing a chromogenic material in an organic solvent and a color developer being provided outside of said microcapsules, in which record material the microcapsules, which comprise an integral outer wall material and an open-core sponge-like networked core extending from the wall material into the microcapsule and defining a plurality of substantially discrete but extensively interconnected void spaces, have been formed by reaction in the presence of a dispersion of the chromogenic material-containing organic solvent of an excess, compared to a stoichiometric amount, of a polyisocyanate having a functionality greater than two with an active hydrogen-containing compound.

The invention also provides a microcapsule comprising an integral outer wall material and an open-pore sponge-like networked core extending from the wall material into the microcapsule and defined by a plurality of substantially discrete but extensively interconnected void spaces, and a core material filling said void spaces, said microcapsule having been formed by reaction in the presence of a dispersion of the core material, of an excess, compared to a stoichiometric amount for effecting encapsulation, of a polyisocyanate having a functionality greater than two with an active hydrogen-containing compound. Such microcapsules when for use in record material as above contain a chromogenic material.

Preferably the microcapsules are of less than 500 microns diameter and have a void volume of 60 to 80% by volume.

Particular polyisocyanates and active hydrogen compounds are referred to later herein in the text and claims, together with preferred color developers and chromogenic materials.

General Discussion

The application of the invention, within the above statement, is considered generally below.

The invention may be applied to record material in the form of sheets coated with color-forming systems comprising chromogenic material and acidic color developer. It particularly concerns a thermally-responsive record material containing crosslinked internal phase microcapsules, said microcapsules having a spongelike cross-linked networked structure extending from the wall material into the core of the capsules, either filling them or leaving an internal space.

The recording layer of the record material comprises, in a single layer or one or more sublayers, microcapsules containing a chromogenic material and an organic solvent in the core of the microcapsules. A color developer is included outside of the microcapsules in the recording layer or as a separate layer. The color developer is suitably selected to be an acidic material or electron pair acceptor. Such materials react with the chromogenic material to form a mark. The microcapsules have wall material which is the reaction product of an excess of an aliphatic polyisocyanate with an active hydrogen containing compound. Additionally, the microcapsules have a thickened wall in that they have a cross-linked network structure extending from, and of, the wall material, extending substantially into the core of the microcapsules. This results in the microcapsules having a spongelike internal core. The spongelike internal core is an open core network structure extending from or of the wall material. Like a chain of interconnected lakes, the networked or spongelike core is defined by a plurality of substantially discrete but extensively interconnected void spaces.

Capsules can be made by interfacial polymerization, for example by using an internal phase of chromogen, (preferably up to about 3.38 parts of a fluoran compound); solvent, (preferably up to about 8 parts diphenyl methane and up to about 18.63 parts secondary butyl biphenyl), and an aliphatic polyisocyanate wall-forming material (preferably about 4.00 parts polyisocyanate). A catalyst (preferably up to about 0.5 parts dimethyl tin dilaurate) can optionally be employed.

The aliphatic polyisocyanate is preferably selected to be a trimer isocyanate.

The above-described internal phase is emulsified in an emulsifying aid, a protective colloid such as a mixture of low and high viscosity polyvinyl alcohol (preferably up to about 2.5 parts) low viscosity polyvinyl alcohol (20% solids), and (preferably up to 3 parts) high viscosity polyvinyl alcohol (10% solids), and distilled water (about 30 parts). In a preferred embodiment, when the capsule diameter reaches approximately 10 µm, pentaethylenehexamine (PEHA) (about 3 parts 100% solids) is added along with 50 parts distilled water. Stirring is continued for 24 hours at 50°C. In place of PEHA, multifunctional amines (about 3 parts of 100% solids) can be optionally employed and include the following: tetraethylenepentamine; bis-(hexamethylene)triamine; or N,N′-bis(3-aminopropyl)ethylenediamine, or polyethylenimine at 50% solids. Pentaethylenehexamine is preferred.

Brief Description of Drawings

Figures 1,2, and 3 are photographs of cross-sectioned microcapsules according to the invention at 37.5 x 27 x and 27 x magnification respectively. The photographs show the spongelike networked core structure extending from the wall material substantially into the interior of the capsule.

In Fig.1 the integral outer wall or shell of the microcapsule is evident on the horizon of the half sphere of the capsule shown.

The Fig 2 cross-section shows the spongelike core filling the interior of a microcapsule.

The Fig. 3 cross-section shows the spongelike core extending substantially into but no filing the entire interior of the microcapsule.

More Detailed Description

The microcapsules have a networked polymeric structure, spongelike in appearance extending substantially into the interior of the microcapsule. They show core thickening (i.e. wall thickening via a spongelike network) from the isocyanate crosslinking. Thermal record materials using such capsules have improved smudge resistance.

The capsules are suitably a reaction product of a polyisocyanate having a functionality greater than two, with an active hydrogen-containing compound. The active hydrogen-containing compound can include alcohols, amines, or water. Typically such compounds include polyethylenimine or polyvinylalcohol. The polyisocyanate is used in excess of the quantity of polymeric reactant conventionally employed to form capsules for carbonless paper, which typically is less than 5% of the total capsule mass. In a departure from the past, in capsules of the invention, the polyisocyanate is employed and is deliberately selected to be used in excess of the stoichiometric amount needed for encapsulation; more particularly it may be used in excess in a concentration of 10-30%, preferably 15% by weight of the total capsule mass.

The isocyanates can participate in several reaction pathways with active hydrogen containing compounds including:

with alcohols:

$$R{-}N{=}C{=}O \; + \; R^1OH \; \rightarrow \; R{-}HN{-}\underset{\underset{O}{\|}}{C}{-}OR^1$$

with amines

$$R{-}N{=}C{=}O \; + \; R^1{-}NH_2 \; \rightarrow \; R{-}HN{-}\underset{\underset{O}{\|}}{C}{-}NH{-}R^1$$

with water

$$R{-}N{=}C{=}O \; + \; H_2O \; \rightarrow \; R{-}NH{-}\underset{\underset{O}{\|}}{C}{-}OH$$

$$\downarrow \quad \text{degrades}$$

$$R{-}NH_2{+}CO_2$$

$$\downarrow \quad + \; R^1{-}N{=}C{=}O$$

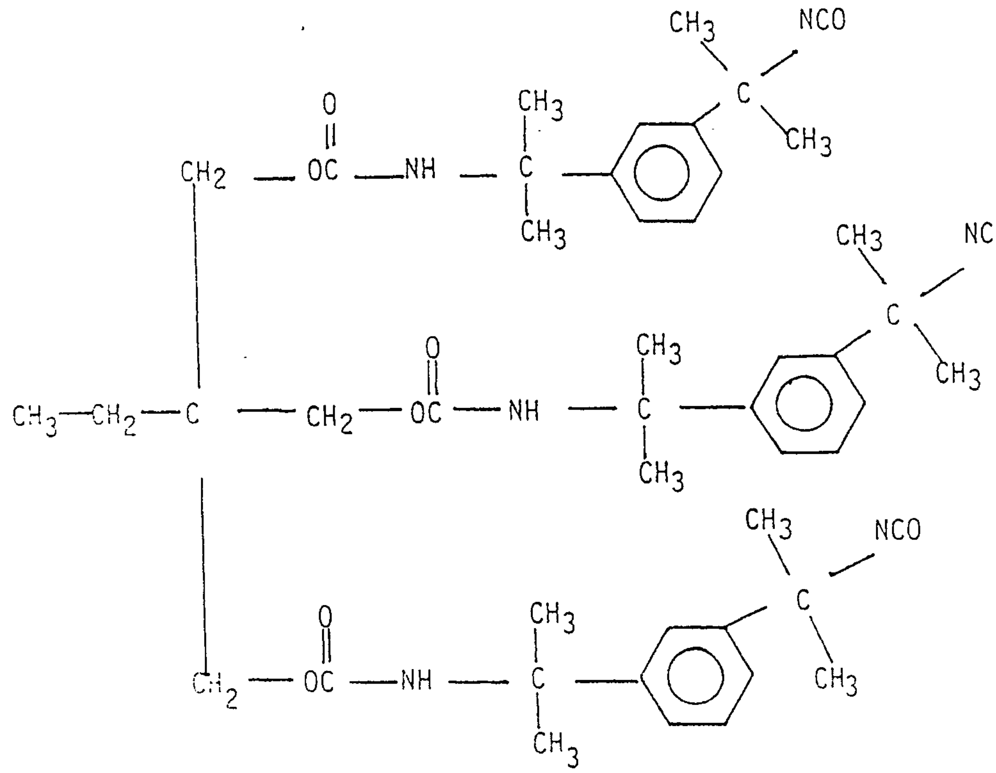
$$R{-}HN{-}\underset{\underset{O}{\|}}{C}{-}NH{-}R^1$$

The isocyanates are more particularly aliphatic polyisocyanates having a functionality of more than one, preferably a functionality of three. A functionality of two optionally can be employed if for example the other monomer is selected to have a functionality of three. A diisocyanate with a functionality of two, for example, can give rise to extension of the three dimensional network once branching with a trifunctional monomer has initiated. Monomers with functionality of two can be utilized to propagate network structures into the interior of the capsule core, though further cross-linking of course would then not be promoted through such monomer.

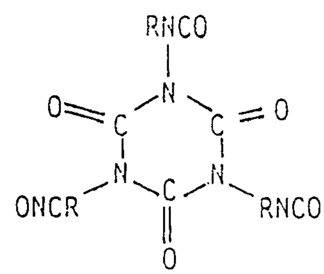
The microcapsules have a networked polymeric structure extending substantially into the interior of the microcapsules. This network core is a spongelike thickening of the wall material in appearance defined by a plurality of discrete extensively interconnected void spaces. This thickening of the wall material is visually observable when cross-sections are made, particularly of the larger microcapsules. Thermal record materials made using these capsules are resistant to smudge. The polymeric structure extending from the wall material substantially into the core of the microcapsules is indirectly observable by the core contents exhibiting higher viscosity. A cross-sectioned capsule observed under magnification when poked with a blunt instrument deforms and exudes core contents (internal phase solvent) through cracks in the crosslinked IP (internal phase) material but immediately receding into the microcapsule upon release of the applied pressure.

The aliphatic polyisocyanates may be of formula OCNRNCO or dimers or trimers thereof wherein R is a substituted or an unsubstituted aliphatic group of 1 to 12 carbons. A convenient formula for these isocyanates is $(OCNRNCO)_y$ wherein y is 1 to 3, R as above defined, it being understood that dimerization or trimerization takes place via the reactive carbons and/or nitrogens. Oligomers of the aliphatic polyisocyanates can also be advantageously employed. By oligomer it is understood to include polymeric chains of the trimer or dimer or isocyanate up to 10 units thereof, i.e. $[(OCNRNCO)_y]_x$ wherein x is an integer from one to 10. Typical of such aliphatic polyisocyanates are trimethylene diisocyanate; tetramethylene diisocyanate, propylene-1,2-diisocyanate, butylene-1,2-diisocyanate, ethylidene diisocyanate, cyclohexyl-1,4-diisocyanate, hexamethylene-1,6-diisocyanate, and include isocyanurate modified polyisocyanates such as whose preparation is described in U.S. 4,324,879. Useful isocyanates however also include aromatic isocyanates such as 1,4-xylene diisocyanate and m-xylene diisocyanate.

Useful aliphatic polyisocyanates include aliphatic polyisocyanate resins. An example would be

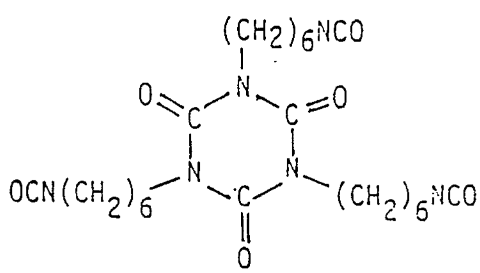


Useful aliphatic polyisocyanates include dimers and trimers of all of the foregoing. Particularly useful are trimers of alkyldiisocyanates such as



wherein R is an aliphatic group of 1 to 12 carbons.

More preferable are trimers of hexamethylene diisocyanate such as



In a preferred process capsules are formed by interfacial polymerization. The resulting condensation polymer is formed by the reaction of a film forming aliphatic polyisocyanate used in excess with a polyvinylalcohol and polyethylenehexamine in presence of a catalyst. While catalyst is not always necessary, conventional isocyanate reaction promoting or urethanation catalyst can be advantageously employed. Dimethyl tin dilaurate catalyst is preferred.

Film forming aliphatic polyisocyanates are known in the art and available commercially. Eligible polyisocyanates include those marketed by Bayer under tradenames Desmodur TT, L, N, R and M; by Mobay Chemical Company as Desmodur N-100, N-3200, N-3300, by Rhone-Poulenc as HDT, HDB, and HDTLV. Polyisocyanates having a molecular weight above about 500 are more desirable.

The material encapsulated, or in other words, contained within the capsule walls formed i.e., the capsular internal phase or core material of the capsule can be any material which is substantially water-insoluble. A few of the materials which can be utilized as capsule internal phases include, among a multitude of others: water-insoluble or substantially water-insoluble liquids, such as conventional carbonless microcapsule internal phase solvents, oils, mineral oil, xylene, toluene, kerosene, diphenylmethane, sec-butylbiphenyl, chlorinated biphenyl, methyl salicylate, along with color formers or dyes such as leuco or fluoran dyes.

Solvents such as diphenylmethane and sec-butylbiphenyl are preferred. The solvent employed can be any material which has sufficient solubility for the color former material, and which does not suppress or otherwise adversely affect the color-forming reaction. Examples of eligible solvents include, but are not limited to, those solvents conventionally used for carbonless copy paper, including ethyldiphenylmethane (U.S. Patent No. 3,996,405); benzyxylenes (U.S. Patent No. 4,130,299); alkylbiphenyls such as propylbiphenyl (U.S. Patent Nos. 3,627,581) and butylbiphenyl (U.S. Patent No. 4,287,074); dialkyl phthalates in which the alkyl groups thereof have from 4 to 13 carbon atoms, e.g. dibutyl phthalate, dioctylphthalate, dinonyl phthalate and ditridecylphthalate; 2,24-trimethyl-1,3-pentanediol diisobutyrate (U.S. patent No. 4,027,065); C_{10}-C_{14} alkyl benzenes such as dodecyl benzene; alkyl or aralkyl benzoates such as benzyl benzoate; alkylated naphthalenes such as dipropylnaphthalene (U.S. patent No. 3,806,463); partially hydrogenated terphenyls; high-boiling straight or branched chain hydrocarbons; and mixtures of the above. The solvents can be solid or liquid. Solids can be encapsulated as melted liquids if desired.

The isocyanate is first dissolved in the core material of what will subsequently become the capsule and the resulting organic phase emulsified in the continuous aqueous phase containing protective colloid and, optionally, emulsifiers. An aqueous active hydrogen containing compound such as a polyamine solution is added to the resulting emulsion in a stoichiometric quantity sufficient to effect encapsulation, based on the normal amount for encapsulation polyisocyanate in the organic phase. The polyisocyanate is kept in excess of the stoichiometric amount needed for encapsulation. The active hydrogen containing compound can be selected from water, polyvinyl alcohol or an aliphatic multifunctional amine.

The core material can be a synthetic or natural solvent or oil along with the color former which is a chromogenic material. Additional examples of oils or solvent which dissolve the chromogenic material include chlorinated biphenyl, chlorinated paraffin, cottonseed oil, peanut oil, silicone oil, phthalate esters, phosphate esters, sulphonate esters, monochlorobenzene, also partially hydrogenated terphenyls, alkylated diphenyls, alkylated naphthalenes, aryl ethers, aryl alkyl esters, higher-alkylated benzene and others which may be used either individually or in combination.

Diluents such as, for example, kerosene, n-paraffins and isoparaffins are frequently added to the solvents.

To produce the microcapsules by polycondensation, the isocyanate present in excess may be dissolved in the hydrophobic core materials mentioned above and the resulting organic phase emulsified in the continuous aqueous phase which contains protective colloid and, optionally, emulsifiers. An aqueous or water soluble polyamine solution may be added to the resulting emulsion in the organic phase.

Active hydrogen containing compounds suitable for reaction with the isocyanates mentioned include multifunctional amines, namely, aliphatic, primary or secondary polyamines, such as for example polyethylenimine, pentaethylenehexamine, tetraethylenepentamine, bis (hexa methylene) triamine, N,N′-bis (3-aminopropyl) ethylenediamine, 1,2-ethylene diamine, bis-(3-aminopropyl)-amine, hydrazine, hydrazine-2-ethanol, bis-(2-methylaminoethyl)-methylamine, 1,4-diaminocyclohexane, 3-amino-1-methyl-aminopropane, N-hydroxyethyl ethylene diamine, N-methyl-bis-(3-aminopropyl)-amine, 1,4-diamino-n-butane, 1,6-diamino-n-hexane, 1,2-ethylene diamine-N-ethyl sulphonic acid (in the form of an alkali salt); 1-aminoethyl-1,2-ethylene diamine and bis-(N,N′-aminoethyl)-1,2-ethylene diamine. Hydrazine and its salts are also regarded as diamines in the present context.

To emulsify and stabilize the emulsion formed, protective colloids and emulsification aids can be added to the aqueous phase. Example of such products acting as protective colloids are carboxymethyl cellulose, gelatin and polyvinyl alcohol. Examples of emulsifiers are ethoxylated 3-benzyl hydroxy biphenyl, reaction products of nonyl phenol with different quantities of ethylene oxide and sorbitan fatty acid esters.

The microcapsules may be produced continuously or in batches. Dispersion machines capable of generating a shear gradient are generally used. Example of such machines are high-speed stirrers, colloid mills, homogenisers, and ultrasonic dispersers. The intensity of the turbulence generated during mixing is a determining factor for the diameter of the microcapsules obtained.

The microcapsules conveniently have a void volume of 60 to 80% by volume. Void volume herein refers to the plurality of void spaces in the spongelike network of the microcapsule interior. The void spaces, of course it is understood will be filled with the ingredients, solvent, chromogen etc., chosen to be encapsulated.

The void volume can be conveniently calculated by a variety of conventional methods. For example, the formed microcapsules can be weighed, the diameter measured and volume calculated. The capsules then can be compressed to exude the contents, selected to be a uniform solvent only. The microcapsules or contents can be separately reweighed. Based on the weight and density of the solvent, or weight and density of the wall material, the volume occupied and therefore the void volume is readily ascertainable.

The microcapsules have a integral outer wall. On visual observation this wall appears substantially continuous. Of course it can be degraded, dissolved, or melted by the environment in which the capsule is situated. Material selection more so determines the mode of capsule disintegration as would be apparent to those skilled in the art. It is from the wall inward that the open pore network structure is substantially developed.

The capsules can be single oil drops or agglomerates and have a narrow particle size distribution. The ratio by weight of core material and sponge-like network to shell material is from 75-90 to 25-10, for preference.

In the process, preferably, the formulations for producing the microcapsules are adjusted in such a way that suspensions containing from 10 to 60% by weight of capsules are obtained.

The polymerization reaction is a polycondensation conducted at a starting pH which is acidic, around pH of 5. As reaction proceeds, alkalinity increases to about pH 7. With use of amines the pH increases to above about 9. The time and temperature requirements are variable to optimize the reaction. The pH need not be specifically modified as reaction proceeds even under the developing alkaline conditions.

After the reaction has progressed to the point where the capsule walls have been solidified and, in that respect, the capsule manufacture is completed, the capsules can be separated from the manufacturing vehicle by filtering and then washed with water. The capsule walls are dried by placing the capsules in a forced air dryer. It should be understood, however, that the capsules need not have dried walls or even be separated from the liquid vehicle prior to their use. If it is desired or required for some intended purpose, the capsule product can be supplied as a slurry of capsules in a liquid carrier, either with the manufacturing vehicle or not, such as for use in a paper coating composition, or the like.

Individual capsules are substantially spherical, readily manufactured having diameters of less than 1 micron to about 100 microns, the preferred size range being from about 1 to about 10 microns, in diameter.

The heat-sensitive record system includes a substrate or support material which is generally in sheet form.

Sheets can be referred to as support members and are understood to also mean webs, ribbons, tapes, belts, films, cards and the like. Sheets denote articles having two large surface dimensions and a comparatively small thickness dimension. The substrate or support material can be opaque, transparent or translucent and could, itself, be colored or not. The material can be fibrous including, for example, paper and filamentous synthetic materials. It can be a film including, for example, cellophane and synthetic polymeric sheets cast, extruded, or otherwise formed. Invention resides in the color-forming composition coated on the substrate. The kind or type of substrate material is not critical.

The components of the color-forming system are in a proximate relationship meaning, a substantially contiguous or near contiguous relationship, substantially homogeneously distributed throughout the coated layer or layers of material deposited on the substrate. In manufacturing the record material, a coating composition is prepared which includes a fine dispersion of the components of the color-forming system, binder material typically a polymeric material, surface active agents and other additives in an aqueous coating medium. The composition can additionally contain inert pigments, such as clay, talc, aluminum hydroxide, calcined kaolin clay and calcium carbonate; synthetic pigments, such as ureaformaldehyde resin pigments; natural waxes such as Carnuba wax; synthetic waxes; lubricants such as zinc stearate; wetting agents; defoamers, and antioxidants. Clearly the components of the color-forming system can be assembled in one layer or with individual components partially or full segregated into multiple layers, such configuration being readily apparent to the skilled worker in the field.

The color-forming system components are substantially insoluble in the dispersion vehicle (preferably water) and except for the microcapsules are ground to an individual average particle size of between about 0.3 micron to about 10 microns, preferably about 1-3 microns. A binder can be included. The binder can be a polymeric material and is substantially vehicle soluble although latexes are also eligible in some instances. Preferred water soluble binders include polyvinyl alcohol, hydroxy ethylcellulose, methylcellulose, methyl-hydroxypropylcellulose, starch, styrene maleic anhydride salts, modified starches, gelatin and the like. Eligible latex materials include polyacrylates, styrene-butadiene-rubber latexes, polyvinylacetates, polystyrene, and the like. The polymeric binder is used to protect the coated materials from brushing and handling forces occasioned by storage and use of thermal sheets. Binder should be present in an amount to afford such protection and in an amount less than will interfere with achieving reactive contact between color-forming reactive materials.

Coating weights can effectively be about 3 to about 9 grams per square meter (gsm) and preferably about 5 to about 6 gsm. The practical amount of color-forming materials is controlled by economic considerations, functional parameters and desired handling characteristics of the coated sheets.

Eligible chromogenic compounds, such as the phthalide, leucauramine and fluoran compounds, for use in the color-forming system are well known color-forming compounds. Examples of the compounds include Crystal Violet Lactone (3,3-bis(4-dimethylaminophenyl)-6-dimethylaminophthalide, U.S. Patent No. Re. 23,024); phenyl-, indol-, pyrrol-, and carbazol-substituted phthalides (for example, in U.S. Patent Nos. 3,491,111; 3,491,112; 3,491,116; 3,509,174); nitro-, amino-, amido-, sulfonamido-, aminobenzylidene-, halo-, anilino-substituted fluorans (for example, in U.S. Patent Nos. 3,624,107; 3,627,787; 3,641,011; 3,642,828; 3,681,390); spirodipyrans (U.S. Patent No. 3,971,808); and pyridine and pyrazine compounds (for example, in U.S. Patent Nos. 3,775,424 and 3,853,869). Other specifically elegible chromogenic compounds, not limiting the invention in any way, are: 3-diethylamino-6-methyl-7-anilino-fluoran (U.S. Patent No, 3,681,390); 2-anilino-3-methyl-6-dibutylamino-fluoran (U.S. Patent 4,510,513) also known as 3-dibutylamino-6-methyl-7-anilino-fluoran; 3-dibutylamino-7-(2-chloroanilino)fluoran; 3-(N-ethyl-N-tetrahydrofurfurylamino)-6-methyl-7-3,5′6-tris(dimethylamino)spiro[9H-fluorene-9,1′(3′H)-isobenzofuran]-3′-one; 7-(1-ethyl-2-methylindol-3-yl)-7-(4-diethylamino-2-ethoxyphenyl)-5,7-dihydrofuro[3,4-b]pyridin-5-one (U.S. Patent No. 4,246,318); 3-diethylamino-7-(2-chloroanilino)fluoran (U.S. Patent No. 3,920,510); 3-(N-methylcyclohexylamino)-6-methyl-7-anilinofluoran (U.S. Patent No. 3,959,571); 7-(1-octyl-2-methylindol-3-yl)-7-(4-diethylamino-2-ethoxyphenyl)-5,7-dihydrofuro-3,4-b]pyridin-5-one; 3-diethylamino-7,8-benzofluoran; 3,3-bis(1-ethyl-2-methylindol-3-yl)phthalide; 3-diethylamino-7-anilinofluoran; 3-diethylamino-7-benzylaminofluoran; 3′-phenyl-7-dibenzylamino-2,2′-spirodi-[2H-1-benzopyran] and mixtures of any of the foregoing.

Examples of eligible acidic developer material include the compounds listed in U.S. Patent No. 3,539,375 as phenolic reactive material, particularly the monophenols and diphenols. Eligible acidic developer material also includes, without being considered as limiting, the following compounds which may be used individually or in mixtures: 4,4′-isopropylidinediphenol (Bisphenol A); p-hydroxybenzaldehyde; p-hydroxybenzophenone; p-hydroxypropiophenone; 2,4-dihydroxybenzophenone; 1,1-bis(4-hydroxyphenyl)-cyclohexane; salicyanilide; 4-hydroxy-2-methylacetophenone; 2-acetylbenzoic acid; m-hydroxyacetanilide; p-hydroxyacetanilide; 2,4-dihydroxyacetophenone; 4-hydroxy-4′-methylbenzophenone; 4,4′-dihydroxybenzophenone; bis(3-allyl-4-hydroxyphenyl)sulfone, 2,2-bis(4-hydroxyphenyl)-4-methylpentane; benzyl 4-hydroxyphenyl ketone; 2,2-bis(4-hydroxyphenyl)-5-methylhexane; ethyl-4,4-bis(4-hydroxyphenyl)-pentanoate; isopropyl-4,4-bis(4-hydroxyphenyl)pentanoate; methyl-4,4-bis(4-hydroxyphenyl)pentanoate; allyl-4,4-bis(4-hydroxyphenyl)pentanoate; 3,3-bis(4-hydroxyphenyl)-pentane; 4,4-bis(4-hydroxyphenyl)-heptane; 2,2-bis(4-hydroxyphenyl)-1-phenylpropane; 2,2-bis(4-hydroxyphenyl) butane; 2,2′-methylene-bis(4-ethyl-6-tertiarybutylphenol); 4-hydroxycoumarin; 7-hydroxy-4-methylcoumarin; 2,2′-methylene-bis(4-octyl phenol); 4,4′-sulfonyldiphenol; 4,4′-thiobis(6-tertiarybutyl-m-cresol); methyl-p-hydroxybenzoate; n-propyl-p-hydroxybenzoate; benzyl-p-hydroxybenzoate; 4-(4-(1-methylethoxy)phenyl) sulphonyl phenol. Preferred among these are the phenolic developer compounds. More preferred among the phenol compounds are 4,4′-isopropylindinediphenol, ethyl-4,4-bis(4-hydroxyphenyl)-pentanoate, n-propyl-4,4-bis(4-hydroxyphenyl)-pentanoate, isopropyl-4,4-bis(4-hydroxyphenyl)pentanoate, methyl-4,4-bis(4-hydroxyphenyl)pentanoate, 2,2-bis(4-hydroxyphenyl)-4-methylpentane, p-hydroxybenzophenone, 2,4-dihydroxybenzophenone, 1,1-bis(4-hydroxyphenyl)cyclohexane, and benzyl-p-hydroxybenzoate; 4-(4-(1-methylethoxy)phenyl) sulphonyl phenol and 4,4′-[1,3-phenylenebis(1-methylethylene]bisphenol. Acid compounds of other kind and types are eligible. Examples of such other compounds are phenolic novolak resins which are the product of reaction between, for example, formaldehyde and a phenol such as an alkylphenol, e.g., p-octylphenol, or other phenols such as p-phenylphenol, and the like; and acid mineral materials including colloidal silica, kaolin, bentonite, attapulgite, hallosyte, and the like. Some of the polymers and minerals do not melt but undergo color reaction on fusion of the chromogen. Of the foregoing particularly the phenol type of compounds are more preferable acidic developer materials.

A modifier (also known as a sensitizer) such as a 1,2-diphenoxyethane can be included. However, the capsule solvent acts as a modifier. A modifier typically does not impart any image on its own but facilitates reaction between the mark-forming components. Modifiers are described in U.S. patent No. 4,531,140. Other modifiers for example include acetoacet-o-toluidine, phenyl-1-hydroxy-2-naphthoate, dibenzyloxalate, diphenoxy ethane and parabenzylbiphenyl. The person of ordinary skill in this art appreciates the modifier or the solvent can be a low melting point solid.

The following example is given to illustrate some of the features of the present invention but should not be considered as limiting. Parts or proportions are by weight and measurements are in the metric system.

A dispersion of a particular system component (unencapsulated) was prepared by milling the component in an aqueous solution of the binder until a particle size of between about 1 micron and 10 microns was achieved. The milling was accomplished in an attritor.

The desired average particle size was about 1-3 microns.

Example

Interfacial capsules were made using an internal phase of 3.38 parts fluoran based color forming agent, 8.00 parts diphenyl methane, 18.63 parts secondary butyl biphenyl, 4.00 parts aliphatic polyisocyanate (HDT or N-3300) and 0.50 parts dimethyl tin dilaurate catalyst. This internal phase was emulsified in a mixture of 2.50 parts low viscosity polyvinyl alcohol (20% solids), 3.00 parts high viscosity polyvinyl alcohol (10% solids), and 30.00 parts distilled water until the capsule size was under 10µm, then 3.00 parts PEHA (100% solids) was slowly mixed into the emulsion. Fifty (50) parts distilled water was added to the emulsion which was then stirred for 24 hours at 50 °C.

The thermally-sensitive coating consisted of 2.91 parts capsules, 2.30 parts medium viscosity polyvinyl alcohol (10% solids), 1.17 parts small media milled coreactant, 0.20 parts zinc stearate, 0.50 parts filler material and 17.93 parts distilled water. The coating was applied to 34 lb./ream base stock paper to get an 8 lb. coating/ream layer. Test results showed Macbeth image intensities of 1.30 in combination with opacimeter readings of 91.3 for frictional smudge, 100.0 for static smudge and 86.6 for background brightness.

A CB coating was made that consisted of 2.91 parts capsule, 5.00 parts starch binder (10% solids), 0.75 parts stilt starch, 0.48 parts clay filler and 16.97 parts distilled water. This coating was applied to 34.5 lb./ream base stock paper to get a 6.0 lb. coating/ream layer. Test results showed an opacimeter measured typewriter intensity of 95.0, frictional smudge of 91.0 and static smudge of 100.0 against a standard CF. Based on past experience this combination of functionalities would be indicative of a high viscosity (i.e. thickened) internal phase capsule.

When large 3-4mm sized capsules were made, a sponge-like network, defined by a plurality of discrete extensively interconnected void spaces, from the wall material extending into the capsules was visibly evident upon cross-sectional examination.

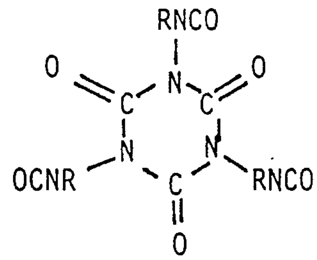
The principles, preferred embodiments, and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes can be made by those skilled in the art without departing from the spirit and scope of the invention as claimed.

Claims

1. A heat sensitive record material comprising a support and a recording layer, said recording layer comprising microcapsules containing a chromogenic material in an organic solvent and a color developer being provided outside of said microcapsules, in which record material the microcapsules, which comprise an integral outer wall material and an open-pore sponge-like networked core extending from the wall material into the microcapsule and defining a plurality of substantially discrete but extensively interconnected void spaces, have been formed by reaction in the presence of a dispersion of the chromogenic material-containing organic solvent of an excess, compared to a stoichiometric amount, of a polyisocyanate having a functionality greater than two with an active hydrogen-containing compound.

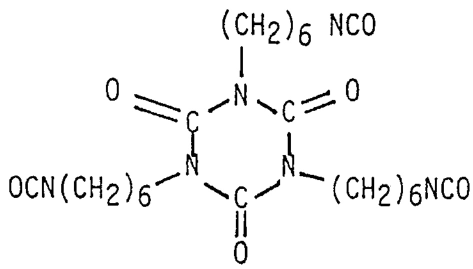
2. A record material according to claim 1 wherein the polyisocyanate is an aliphatic polyisocyanate monomer of 1-12 carbons, or a dimer or a trimer thereof.

3. A record material according to claim 1 wherein the polyisocyanate is

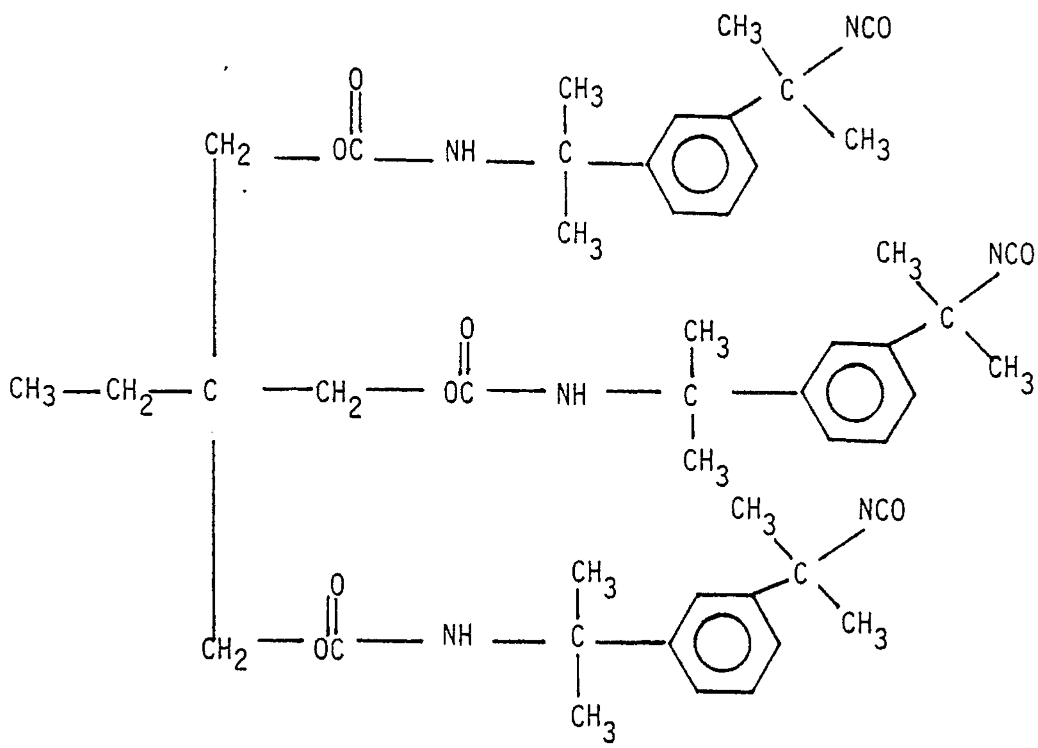


wherein R is substituted or unsubstituted aliphatic group of 1 to 12 carbons.

4. A record material according to claim 1 wherein the polyisocyanate is



5. A record material according to claim 1 wherein the polyisocyanate is



6. A record material according to any preceding claim wherein the active hydrogen containing compound is water, polyvinyl alcohol, or an aliphatic multifunctional amine.

7. A record material according to claim 6 wherein the active hydrogen containing compound is polyethyelenimine.

8. The record material of any preceding claim in which the colour developer material is a phenol compound.

9. The record material of claim 8 in which the color developer is a phenol compound selected from the group consisting of 4,4′-isopropylindinediphenol, ethyl-4,4-bis(4-hydroxyphenyl)pentanoate, n-propyl-4,4-bis-

(4-hydroxyphenyl)pentanoate, isopropyl-4,4-bis(4-hydroxyphenyl) pentanoate, methyl-4,4-bis-(hydroxyphenyl)pentanoate, 2,2-bis(4-hydroxyphenyl)-4-methylpentane, p-hydroxybenzophenone, 2,4-dihydroxybenzophenone, 1,1-bis(4-hydroxyphenyl)cyclohexane, 2,2-bis(4-hydroxyphenyl)-5-methylhexane, benzyl-p-hydroxybenzoate, and mixtures thereof.

10. The record material of any preceding claim, the chromogenic material being from the group consisting of 3-diethylamino-6-methyl-7-anilinofluoran; 7-(1-ethyl-2-methylindol-3-yl)-7-(4-diethylamino-2-ethoxyphenyl)-5,7-dihydrofuro[3,4-b]pyridin-5-one; 3-diethylamino-7-(2-chloroanilino)fluoran; 3-(N-methylcyclohexylamino)-6-methyl-7-anilinofluoran; 7-(1-octyl-2-methylindol-3-yl)-7-(4-diethylamino-2-ethoxyphenyl)-5,7-dihydrofuro-[3,4-b]pyridin-5-one; 3′-phenyl-7-dibenzylamino-2,2′-spiro-di-[2H-1-benzopyran]; 3-dibutylamino-6-methyl-7-anilinofluoran; 3-(N-ethyl-N-tetrahydrofurfurylamino)-6-methyl-7-anilinofluoran; 3-dibutylamino-7-(2-chloroanilino)fluoran; 3,3-bis(4-dimethylaminophenyl)-6-dimethylaminophthalide;7-(1-ethyl-2-methylindol-3-yl)-7-(4-diethylamino-2-ethoxyphenyl)-5,7-dihydrofuro[3,4-b]pyridine-5-one; 3,5′, 6-tris(dimethylamino)spiro-[9H-fluorene-9,1′(3′H)-isobenzofuran]3′-one, and mixtures thereof.

11. The record material of any preceding claim, wherein the microcapsules are of less than 500 microns diameter and have a void volume of 60 to 80% by volume.

12. A microcapsule comprising an integral outer wall material and an open-pore sponge-like networked core extending from the wall material into the microcapsule and defined by a plurality of substantially discrete but extensively interconnected void spaces, and a core material filling said void spaces, said microcapsule having been formed by reaction in the presence of a dispersion of the core material, of an excess, compared to a stoichiometric amount for effecting encapsulation, of a polyisocyanate having a functionality greater than two with an active hydrogen-containing compound.

13. A microcapsule according the claim 12, said microcapsule being of less than 500 microns diameter and having a void volume of from 60% to 80% by volume.

14. A microcapsule according to claim 12 or 13, wherein the polyisocyanate/active hydrogen compound is as respectively set out in any of claims 2 to 5 or 6 and 7.

15. A microcapsule according to claims 12,13 or 14 containing a chromogenic material.

16. A microcapsule according to claim 15 wherein the chromogenic material is as set out in claim 10.

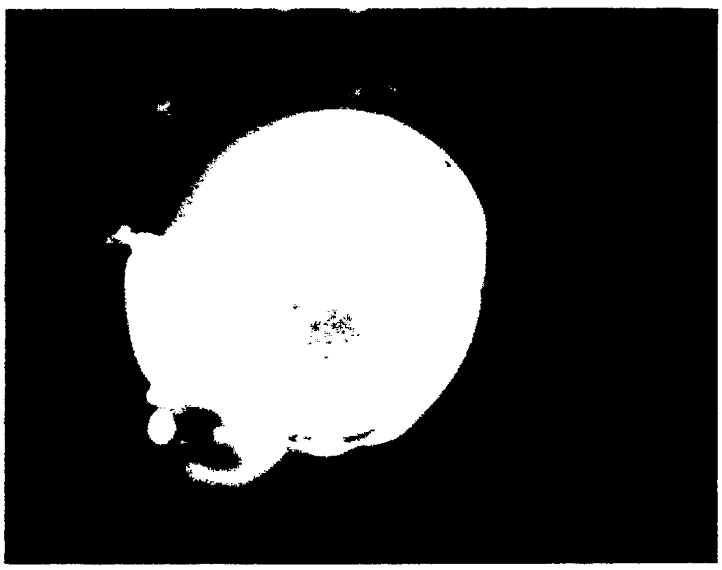


Fig. 1

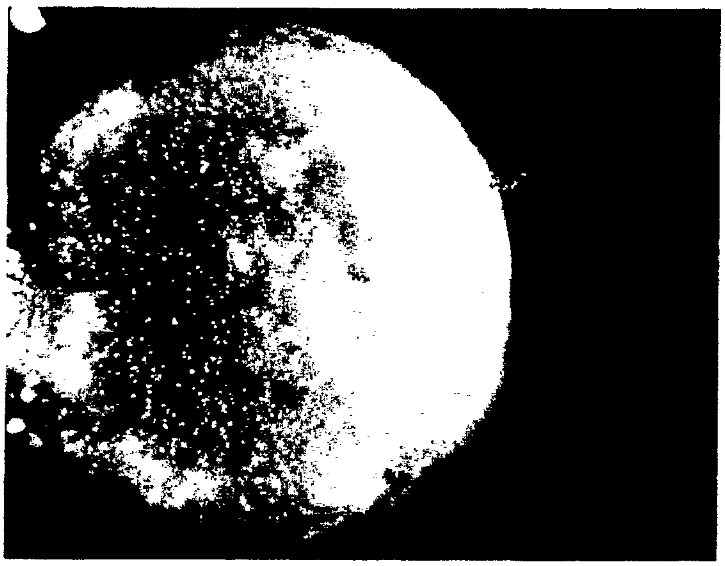


Fig. 2

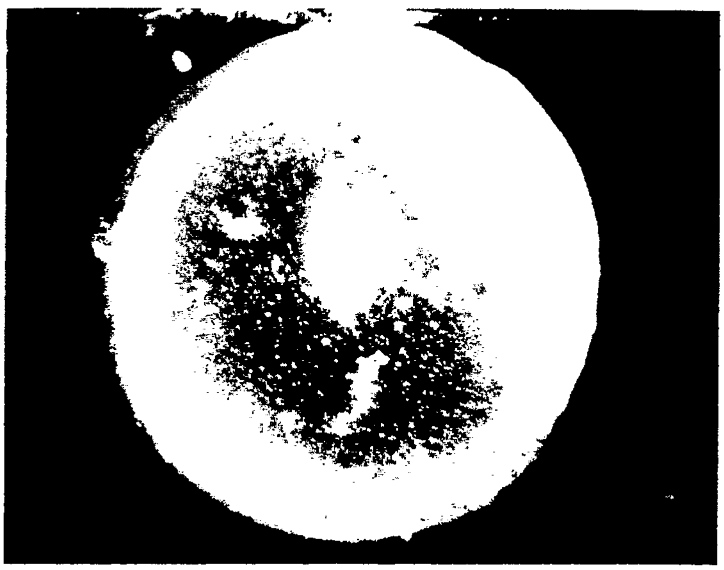


Fig. 3