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(54) **Pressure sensitive copying system.**

(57) A pressure sensitive copying system having comparatively uniform thickness and resistant to smudging, which is suitable for spot-coated copying sheets such as chit is obtained by disposing a color forming components layer on the layer of a microcapsule protective agent which has been provided all over the paper sheet, at least one of the components being enclosed in microcapsules.

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PRESSURE SENSITIVE COPYING SYSTEM

This invention relates to a pressure sensitive copying system and, more particularly, to a pressure sensitive copying system having a microcapsule protective layer and a method for preparing such a copying system.

A pressure sensitive copying system which utilizes the color reaction between an electron donating color former (hereinafter referred to simply as color former) and an electron accepting color developer (hereinafter referred to simply as color developer) has been widely known. In such a system, a color image is formed on a paper sheet by the application of localized pressure to rupture the microcapsule wall separating a color former and a color developer from each other in the presence of a solvent, thus bringing both reactants into contact with each other on the paper sheet to take part in a color-forming reaction.

A typical pressure sensitive copying system is composed of a paper sheet (generally called top sheet) having on one side a layer of microcapsules containing a color former solution and another paper sheet (generally called undersheet) having on one side a layer of a color developer. When the top sheet is placed over the undersheet so that both layers may confront with each other and a localized pressure is applied by means of a writing instrument or the like

to the surface of top sheet, the microcapsules are ruptured to allow a color-forming reaction to take place, forming a color image on the surface of the undersheet. If a sheet (generally called intermediate sheet) having on one side a color former layer and on another side a color developer layer is inserted between the top sheet and the undersheet so that the color developer layer may confront with the color former layer of the top sheet and the color former layer with the color developer layer of the undersheet, a color image can be formed, on applying a localized pressure to the top-sheet, on both color developer bearing surfaces of the intermediate sheet and the undersheet. More copies are obtained by using more intermediate sheets.

There is also a well-known self-contained pressure sensitive copying paper sheet having on one side a layer containing a mixture of the aforementioned three materials participating in causing the color reaction to take place. This sheet also develops color image on application of a localized pressure to said layer.

The foregoing description pertains to a typical pressure sensitive copying system. Among the three materials participating in the color forming reaction, the one which is microencapsulated can be any, so long as any one of the color former, color developer and solvent is kept separated from the others by the microcapsule wall; that is, the material to be encapsulated

can be a color former solution or a color developer solution or, in some circumstances, a solvent alone. The color developer can be microencapsulated as a solution, whether the color former is microencapsulated or not. If the color former is encapsulated, the color developer can be in the form of fine powder. The solvent can be included in either or both of the microcapsules containing the color former and those containing the color developer. The color former and the color developer both in the form of fine powder can be used in combination with microcapsules containing the solvent alone.

A sheet bearing a layer of microencapsulated solvent can be used in combination with a sheet bearing a layer containing both the color former and the color developer, either or both of which may be microencapsulated or not. By arranging both sheets so that both layers may confront with each other, a color iamge is formed on the surface bearing the color former and the color developer by applying a localized pressure. In this case, a plurality of copies can be obtained by coating the other side of a self-contained pressure sensitive copying sheet with microcapsules enclosing the color former and using the resulting sheet in combination with an undersheet. It is understandable that many other variations of the combination are possible by utilizing the color-forming reaction which takes place upon the application of marking pressure in the presence

of a solvent to the system comprising a color former and a color developer which are separated from each other by the wall of microcapsules.

The pressure sensitive copying system described above has been widely used in various business forms, slips, chits, record paper, computer paper, etc. and proved to be useful. For this very reason, however, further improvement in quality has been required in various respects.

One of the disadvantages of the aforementioned pressure sensitive copying system utilizing the ruputure of microcapsules on application of pressure is an accidental rupture of the microcapsules, leading to abnormal color formation (smudging) during the manufacture, printing, and assembling of the copying sheets. The elimination of such a disadvantage has long been required.

To overcome the above difficulty a microcapsule protective agent has been used in admixture with microcapsules in coating the latter on the sheet. Such agents disclosed in various patents include finely powdered cellulose (U.S. Patent 2,711,375), starch particles (Brit. Patent 1,232,347; Japanese Patent Publication Nos. 1,176/72 and 33,204/73), glass beads (U.S. Patent 2,655,453), and thermally expandable polymer particles (microspheres) (Japanese Patent Application Laid-open No. 32,013/73). Those protective agents having a particle size larger than that of microcapsules

are usable if not satisfactorily, while those having a specific gravity different too greatly from that of the microcapsules or having a broad particle size distribution are undesirable, because it is difficult to maintain constancy in the quality of the coated sheet owing to an increased tendency of the microcapsules and the protective agent to segregate gradually in the coating composition while being applied to the sheet. On the other hand, some types of microspheres and granular polyolefins have favorable specific gravities and particle sizes, but they are insufficient in strength and are markedly expensive if a product having a narrow particle size distribution is required. As described above, there are still a number of problems to be solved in using the protective agent.

There is another method for the use of protective agents, characterized in that microcapsules and the protective agent are applied separately to the sheet instead of applying them in a mixture as described above. Japanese Patent Application Laid-open No. 15,709/77 disclosed a method in which microcapsules are coated on the color forming areas and subsequently the protective agent is overlaid. This method has disadvantages in that feathering of the impressed image is apt to occur and that when the coating composition containing microcapsules and the composition containing a protective agent are applied by the method of spot coating by means of printing machine, the coated areas

are increased in thickness and become more sensible to accidental application of pressure, causing difficulty in handling the coated sheets.

An object of this invention is to provide a pressure sensitive copying system suitable for spot-coated copying sheets such as chits.

Another object of this invention is to provide a pressure sensitive copying system having comparatively uniform thickness and resistant to abnormal color formation (smudging).

According to this invention there is provided a pressure sensitive copying system including paper sheets and, disposed thereon in selected areas, a stratum of pressure sensitive color forming composition comprising a combination of an electron donating color former, an electron accepting color developer, and a solvent, at least one of the components of said combination being enclosed in microcapsules which are protected by a microcapsule protective agent, which is characterized in that an underlayer containing the microcapsule protective agent is disposed all over the paper sheet which is to bear said color forming stratum, and a layer containing at least one of the components of said combination is laid over said underlayer in the selected areas.

The pressure sensitive copying system of this invention is manufactured by providing on a paper sheet an underlayer containing a microcapsule protective agent so as to cover entire surface of the paper sheet

and subsequently disposing, by coating or printing, on image forming areas of said underlayer at least one member of the group consisting of an electron donating color former, an electron accepting color developer and a solvent for both of said color former and color developer, at least one of the members of said group being micro-encapsulated.

Thus, in the pressure sensitive copying system of this invention, an underlayer containing a microcapsule protective agent is coated all over the surfaces (including the image forming areas) of the aforementioned top sheet, intermediate sheet and undersheet as well as various other types of copying sheets and said underlayer is overlaid with layers containing the materials participating in the color forming reaction, each alone or in combinations. In a pressure sensitive copying system including a plurality of image forming sheets, at least one of the sheets, preferably the top sheet or the intermediate sheet, can be prepared according to this invention.

Another feature of the present invention is such that either the color former or the color developer can be included in the base sheet or in the layer containing the microcapsule protective agent.

When an encapsulated solvent is used, it is possible to coat both the color former and the color developer on one side of an undersheet or an intermediate sheet and assemble such a sheet together with a top

sheet or an intermediate sheet carrying a layer of the microencapsulated solvent so that the layer of microencapsulated solvent may confront with the layer containing the color former and the color developer. It is also possible to prepare a self-contained pressure sensitive copying sheet by coating one side of a paper sheet with the microencapsulated solvent, a color former and a color developer. In these cases, at least one of the color former and the color developer can be incorporated into the sheet which is to be coated with a microcapsule protective agent or can be coated together with a microcapsule protective agent. In such cases the time required for the image color to reach its maximum density is slightly prolonged and the maximum density is slightly decreased.

When a solution of a color former is microencapsulated, it is possible to coat a color developer on one side of an undersheet or an intermediate sheet and assemble such a sheet together with a top sheet or an intermediate sheet carrying a layer of the microcapsules so that this layer of the microcapsules may confront with the coating layer of the color developer. It is also possible to prepare a self-contained pressure sensitive copying sheet by coating one side of a paper sheet with microcapsules and a color developer. In these cases, the paper sheet to be coated with a microcapsule protective agent can be incorporated with the color developer or coated with the color developer

together with a microcapsule protective agent. In such cases the time required for the image color to reach its maximum density is relatively short and the maximum density is rather high.

Further, when a solution of a color developer is microencapsulated, it is possible to coat a color former on one side of an undersheet or an intermediate sheet and assemble such a sheet together with a top sheet or an intermediate sheet carrying the microcapsules so that the layer of these microcapsules may confront with the color former layer. It is also possible to prepare a self-contained pressure sensitive copying sheet by coating one side of a paper sheet with microcapsules and the color former. In these cases, the paper sheet to be coated with a microcapsule protective agent can be incorporated with the color former or coated with the color former together with the microcapsule protective agent. In such cases the time required for the image color to reach its maximum density is relatively short.

As a variation of the above modes of embodying the present invention, use may be made of a color former solution and a color developer solution, both being microencapsulated. The two kinds of microcapsules are coated as a mixture or in two consecutive layers on an undersheet or on one side of an intermediate sheet having a precoating layer of the color developer or having no such a precoating layer, and the resulting

coated sheets are assembled so that the coating layers may confront with each other. A self-contained pressure sensitive sheet may also be prepared by coating both kinds of microcapsules as a mixture or in two consecutive layers. Many other combinations of the component materials are possible without departing from the spirit and scope of this invention, provided that the base sheet carries a continuous undercoating layer of a microcapsule protective agent.

The reasons for the comparatively uniform thickness of the copying sheet prepared according to this invention by spot-coating an image forming stratum on selected areas of an undercoating of a microcapsule protective agent seem to be a reduced difference in thickness between the image forming areas and the image non-forming areas as well as the penetration of microcapsules into voids between the particles of microcapsule protective agent.

The color former for use in the copying system of this invention can be any compound capable of forming color by reacting with a suitable color developer. Exampels of suitable color formers include triarylmethane compounds such as 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide (generally called crystal violet lactone), 3,3-bis(p-dimethylaminophenyl)phthalide, 3-(p dimethylaminophenyl)-3-(1,2-dimethylindol-3-yl)-phthalide, 3-(p-dimethylaminophenyl)-3-(2-methylindol-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(2-

methylindol-3-yl)phthalide, 3,3-bis(9-ethylcarbazol-3-yl)-5-dimethylaminophthalide, etc.; dimethylmethane compounds such as 4,4'-bisdimethylaminobenzhydrin benzyl ether, N-halophenylleucoauramine, etc.; xanthene compounds such as rhodamine B anilinolactam, 3-dimethylamino-7-methoxyfluorane, 3-diethylamino-7-chlorofluorane, 3-diethylamino-6,8-dimethylfluorane, 3-dimethylamino-7-methylaminofluorane, 3-7-diethylaninofluorane, 3-diethylamino-7-dibenzylaminofluorane, 3-diethylamino-chloroethylmethylaminofluorane, etc.; thiazine compounds such as benzoylleucomethylene blue, p-nitrobenzylleucomethylene blue, etc.; and spiro compounds such as 3-methylspirodinaphthopyrane, 3-ethylspirodinaphthopyrane, 3,3'-dichlorospirodinaphthopyrane, 3-propylspirobenzopyrane, etc. These color formers are used each alone or in mixtures.

The color developers capable of forming color upon reacting with a color former includes inorganic acidic substances such as acid clay, activated acid clay, attapulgite, kaclin, aluminum silicate; phenolic substances such as various alkyl-substituted phenols, 4,4'-(1-methylethylidene)bisphenol, phenol-aldehyde condensation products, etc.; aromatic carboxylic acids such as benzoic acid, chlorobenzoic acid, toluic acid, salicylic acid, 5-tert-butylsalicylic acid, 3,5-di-tert-butylsalicylic acid, 3,5-di(α-methylbenzyl)-salicylic acid, etc.; and metal salts of above-noted aromatic carboxylic acids such as copper, lead, magnesium,

calcium, zinc, aluminum, tin, and nickel salts. These color developers are used each alone or in mixtures.

In enclosing a color former or a color developer within microcapsules, frequently a solution of the color former or color developer in a suitable solvent is microencapsulated. Such solvents are those capable of dissolving color formers and color developers. Suitable known solvents include mineral oils such as kerosene and paraffin oil; animal oils such as fish oil, lard, etc.; vegetable oils such as peanut oil, linseed oil, soybean oil, castor oil, etc.; and synthetic oils such as those of the alkylnaphalene type, diarylalkane type, alkylbiphenyl type, hydrogenated terphenyl type, triaryldimethane type, phenylene oxide type, alkylbenzene type, benzylnaphthalene type, diarylalkylene type, arylindane type, and esters of dibasic fatty acids.

A variety of encapsulation processes have been known, of which famous processes are coacervation (U.S. Patent Nos. 2,800,457, 2,800,458 and 3,041,288; Japanese Patent Publication Nos. 27,227/64 and 43,547/73), interfacial polymerization (Brit. Patent 950,443; U.S. Patent 3,208,951; Japanese Patent Publication Nos. 23,709/68 and 11,772/69) and in situ process (Japanese Patent Publication Nos. 12,380/62 and 30,282/71).

The microcapsule protective agents used in this invention are aforementioned powdered cellulose, starch particles, glass beads, microspheres; polymer particles such as particles of polyolefins, nylon, polyvinyl

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chloride, polymethyl methacrylate and tetrafluoroethylene-hexafluoroethylene copolymers; and inorganic particles such as powdered aluminum, powdered zinc, atomized copper-lead alloy, atomized bronze, powdered titanium, white carbon, calcium carbonate, calcium tungstate and zinc sulfide. Those materials which can be used as protective agents have a larger particle size than that of microcapsules. Preferred are those particles which are spherical in shape and colorless.

The microcapsule protective agents are admixed with proper amounts of suitable binders and, if necessary, other additives and applied to a base paper sheet by a suitable method. Blade coating and air knife coating are generally used in view of productivity and for other reasons. Other known coating methods such as bar coating, rod coating, roller coating, fountain coating, gravure coating, spray coating, dip coating and extrusion coating can also be used.

Microcapsules are admixed with necessary amounts of suitable binders and applied to a base paper sheet having the precoating of microcapsule protective agents. Although blade coating and air knife coating are frequently used similarly to the coating of microcapsule protective agents, other coating methods such as bar coating, rod coating, roller coating, fountain coating, gravure coating, spray coating, dip coating and extrusion coating can be employed. Spot printing is also possible by suitable coating or printing methods.

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The invention is illustrated below with reference to Examples which are presented by way of mere illustration, but not by way of limitation.

Example 1

A dispersion containing 43% of microcapsules, 3.7 nm in average particle diameter, containing a solution of 2% by weight of 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide (crystal violet lactone) in 1-phenyl-1-xylylethane was prepared according to the usual in situ method.

On the other hand, a mixture was prepared from 10 parts by weight of an aqueous solution containing 10% by weight of polyvinyl alcohol (DVA-117 of Kuraray Co.), 10 parts by weight of wheat starch, used as microcapsule protective agent, and 60 parts by weight of water. The mixture was uniformly coated by a coating rod (mayer bar) on a paper sheet at a rate of 1 g/m^2 in terms of solids (after drying at 105°C for 2 minutes).

Next, a mixture was prepared from 10 parts by weight (in terms of solids) of the above microcapsule dispersion and 10 parts by weight of an aqueous solution containing 10% by weight of polyvinyl alcohol. The mixture was overcoated by means of a coating rod on the above paper sheet undercoated with the wheat starch at a rate of 3 g/m^2 in terms of solids after drying at 105°C for 2 minutes. The coated sheet was dried at 105°C for 2 minutes and used as top sheet. The top sheet was

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superposed on a commercial pressure sensitive undersheet (containing a p-phenylphenol resin) and a downward marking pressure was applied to the top sheet by means of a ball-pointed pen to obtain an impression image which was found to be sharp and clear.

A "top sheet" prepared as above was placed with capsule-coated side upward on a flat surface of a table. A commercial "undersheet" was superposed with the coated side downward on the "top sheet". A 300 g metal weight, 10 cm^2 in bottom area, was placed on the "undersheet". After the "top sheet" had been fixed on the table, the "undersheet" carrying the weight was moved horizontally for a distance of 50 cm and the coated side of the "undersheet" was examined for the density of colcr image by means of a color difference meter (supplied by Nippon Denshoku Kogyo Co.) and was found to be 75.5. [Note: The scale on the meter covered from 0 to 100. A smaller figure means a higher color density (the same applies hereinafter)].

Comparative Example 1

This experiment was carried out to demonstrate, by comparison, the effectiveness of the microcapsule protective agent used in Experiment 1.

A "top sheet" was prepared in the same manner as in Example 1, except that the wheat starch was not used. In the same manner as in Example 1, the color density of the image formed by the weight was determined

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by means of a color difference meter and was found to be 39.4, indicating that the use of a microcapsule protective agent is very effective; the color formation due to rubbing was markedly less in Example 1 than in Comparative Example 1.

Example 2

This experiment was carried out to demonstrate that a copying sheet with fairly good profile is obtained from a base sheet provided with an undercoating of a microcapsule protective agent.

A dispersion of microcapsules prepared in the same manner as in Example 1 was spray-dried to obtain a powder. A mixture was prepared by mixing together 50 parts by weight of said microcapsules in powder form, and 50 parts of an ethanol solution containing 12% by weight of ethylcellulose.

The above mixture was coated by means of a rubber printing plate on the right half portion of a paper sheet having an undercoating of wheat starch as in Example 1. Twenty sheets coated in the same manner were superposed one over another so that the coated portion of each sheet may be in the same relative position. The total thickness of the uncoated portions was 1.264 mm, while that of the microcapsule-bearing portions was 1.280 mm, as measured by means of a micrometer, indicating that the difference was very small.

By the addition of an additional amount of the

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microcapsule protective agent to the microcapsule dispersion, there was obtained a color image with more improved neatness and decreased staining.

Comparative Example 2

This experiment was carreid out to demonstrate by comparison with the results obtained in Example 2 that the undercoating of a microcapsule protective agent has advantageous effect on the profile of paper sheets locally coated with microcapsules.

A mixture was prepared by mixing together 40 parts of the capsule powder prepared as in Example 2, 12 parts of wheat starch, and 48 parts of ethanol solution containing 12% by weight of ethylcellulose. The mixture was coated by means of a rubber printing plate on the right half portion of the same paper sheet as used in Example 2. Twenty sheets coated in the same manner were superposed one over another so that the coated portion of each sheet may be in the same relative position. The total thickness of the uncoated portions was 1.183 mm, while that of the microcapsule-bearing portions was 1.274 mm, as measured by means of a micrometer, indicating that the profile of a paper sheet is improved when the microcapsules were spot-printed on the undercoating of a microcapsule protective agent.

Comparative Example 3

This experiment was carried out to compare the

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printing quality of copying sheets prepared by coating a paper sheet with microcapsules and a microcapsule protective agent as a mixture or separately in two consecutive layers.

A top sheet I was prepared in the same manner as in Example 1. A top sheet II was prepared in the same manner as in Example 1, except that the same microcapsule coating composition as used in Example 1 was coated on a paper sheet at a rate of 3 g/m^2 (after drying at 105°C for 2 minutes) and subsequently a wheat starch coating composition was coated over said undercoating at a rate of 1 g/m^2 (after drying at 105°C for 2 minutes). A top sheet III was prepared by coating a paper sheet with a mixture of 10 parts of the same microcapsule coating composition and 8 parts of the same wheat starch coating composition as used in Example 1 by means of a coating rod at a rate of - g/m^2 (after drying at 105°C for 2 minutes).

Each of the top sheets I, II and III was superposed on a commercial undersheet (containing p-phenylphenol resin) and impressed by means of a type with flush face and an IBM-895 typewriter at an intensity 5. The color density of the impressed image was measured as in Example 1. The densities corresponding to I, II and III were 31.5, 33.3 and 31.6, respectively.

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Example 3

This Example relates to a self-contained pressure sensitive copying sheet having an undercoat of a mixture of a color developer and microcapsule protective agents.

A mixture was prepared from 10 parts of aluminum hydroxide, 40 parts of wheat starch, 10 parts (in terms of solids) of a dispersion of p-phenylphenol resin (p-phenylphenol-formaldehyde condensation product), 50 parts of a 10% aqueous solution of polyvinyl alcohol (PVA-117 of Kuraray Co.), and 50 parts of water. A paper sheet was coated by means of a coating rod with the above mixture at a rate of 8 g/m^2 (after drying at 105°C for 2 minutes) and subsequently with the same microcapsule coating composition (admixed with the polyvinyl alcohol solution) as used in Example 1 at a rate of 2 g/m^2 (after drying at 105°C for 2 minutes).

The above self-contained pressure sensitive copying sheet was impressed by means of a type with flush face and an IBM-895 type-writer at an intensity of 5. The color density of the impressed image was found to be 35.1. Further, the color formed due to rubbing was examined as in Example 1. The color density was found to be 81.5, indicating the effectiveness of the microcapsule protective agent.

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CLAIMS

1. A pressure sensitive copying system including paper sheets and, disposed thereon in selected areas, a stratum of pressure sensitive color forming composition comprising a combination of an electron donating color former, an electron accepting color developer, and a solvent, at least one of the components of said combination being enclosed in microcapsules which are protected by a microcapsule protective agent, which is characterized in that an underlayer containing the microcapsule protective agent is disposed all over the paper sheet which is to bear said color forming stratum, and a layer containing at least one of the components of said combination is laid over said underlayer in the selected areas.

2. A pressure sensitive copying system according to Claim 1, wherein the microcapsule-protective agent-containing layer is disposed under the layer of microcapsules enclosing the electron donating color former and the solvent.

3. A pressure sensitive copying system according to Claim 1, wherein a microcapsule-protective agent-containing layer is disposed under the layer containing a mixture of the electron accepting color developer and microcapsules enclosing the electron donating color former and the solvent.

4. A pressure sensitive copying system according to Claim 1, wherein the microcapsule-protective agent-containing layer contains the electron donating color

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former or the electron accepting color developer which is not enclosed by microcapsules and is disposed under the layer containing microcapsules of ether the electron accepting color developer or the electron donating color former.

5. A pressure sensitive copying system according to claim 1, wherein the electron donating color former or the electron accepting color developer which is not enclosed by microcapsules is contained in the paper sheet over which microcapsule-protective agent-containing agent layer is disposed.