June 17, 1969 J. M. BILLET ET AL 3,450,553

PRESSURE SENSITIVE RECORD MATERIAL

Filed Jan. 3, 1966

FIG. 1

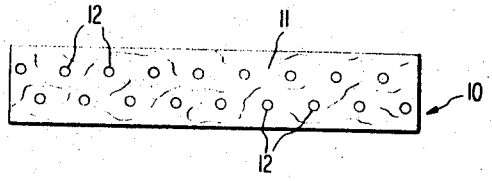


FIG. 2

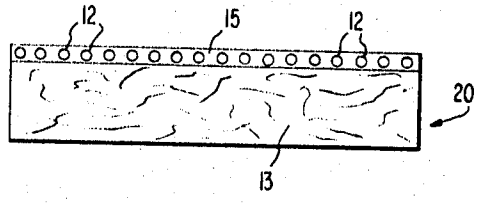


FIG. 3

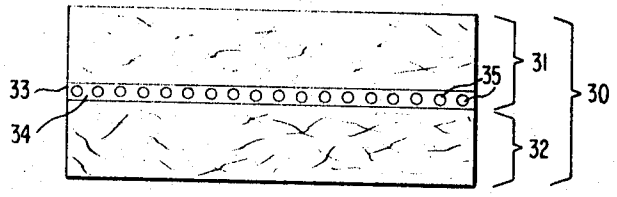
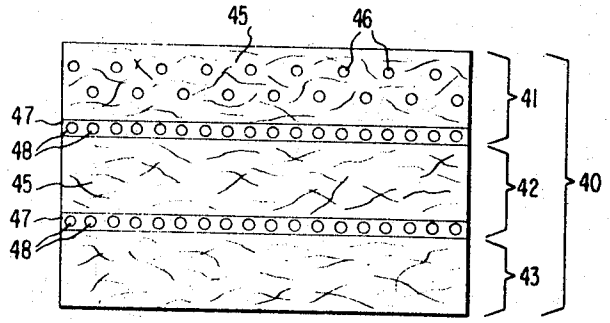


FIG. 4



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PRESSURE SENSITIVE RECORD MATERIAL

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U.S. Cl. 117—36.2 21 Claims

ABSTRACT OF THE DISCLOSURE

A pressure sensitive record material which comprises a sheet of paper containing at least about five percent lignin and a substantially colorless reactant which reacts with lignin under writing pressure to form visible reaction products. The reactant includes phenolic materials such as phloroglucinol, aromatic bases such as aniline hydrochloride, heterocyclic compounds such as 3 - aminopyridine and inorganic compounds such as cobalt, thiocyanate.

The present invention relates to new pressure sensitive record materials. The principles of the invention are adaptable both to single element copy systems and to multiple element arrangements similar to conventional manifolding packs.

The purpose of the invention is to provide reliable pressure sensitive record materials which produce clear and durable copies without the need for using carbon papers or similar transfer materials. A further object of the invention is to provide pressure sensitive record materials which have good shelf life and which are resistant to smudging or smearing as a result of normal handling.

In general, the pressure sensitive record materials of the present invention comprise a sheet of paper containing lignin. A color precursor is associated with the sheet of paper, so that upon the application of pressure, the lignin and the color precursor react to form visible markings. The color precursor may be incorporated in the body of the sheet of paper in a passive form and be rendered active by application of pressure. Alternatively, the color precursor may be carried on the surface of the paper sheet or on the surface of another associated element, so that upon application of pressure the lignin and color precursor are brought together to form the desired reaction products.

The present invention will be more fully appreciated in view of the following detailed description of certain preferred embodiments considered in the light of the accompanying drawing.

In the drawing:

FIGURES 1 and 2 are schematic, cross-sectional, edge views of sheets of record material in accordance with the invention,

FIGURE 3 is a schematic, cross-sectional, edge view of a two-sheet manifolding pack utilizing record material of the present invention, and

FIGURE 4 is a somewhat schematic, cross-sectional, edge view of a four-sheet manifolding pack utilizing record material of the present invention.

The basic element of the pressure sensitive record materials of this invention is a sheet of record material comprising a substantial amount of lignin uniformly distributed throughout or coated on the sheet. The sheet is preferably paper containing residual lignin, but the lignin may be separately added to the paper "on machine," i.e., during the paper forming operation, of "off machine," i.e., at a stage subsequent to the paper formation. The latter would include, e.g., coating, sizing or impregnating the paper with a lignin containing material.

The chemical composition of lignin is not known with precision. Lignin is the major non-carbohydrate constituent of wood and woody plants and may comprise about 25% of such materials. It functions as a natural plastic binder for the cellulosic fibers of wood, straw, etc. Rather than referring to a specific compound, the term lignin actually is a collective term for a group or system of compounds of high molecular weight. A summary of the functional groups and interunit linkages in lignin as it is now known is described by E. Adler in Das Papier 15, page 604 (1961). The color forming group is generally regarded to be the coniferyl aldehyde group.

Paper containing lignin may be readily produced by controlling the pulping action during the paper making process. During the manufacture of paper pulp from wood (there is no lignin in cotton), straw, etc., by the conventional chemical processes, such as the sulfate (kraft), sulfite and soda pulping a certain amount of the hemicelluloses and lignin are removed. In the less expensive types of paper produced by the milder chemical processes commonly referred to as "semi-chemical" or "chemi-ground wood," a very large percentage of the lignin originally present in the original fiber (wood, straw, etc.) is retained in the pulp.

As an example, suitable papers were prepared from the following pulps on the web former of the Institute of Paper Chemistry:

(1) Hardwood unbleached sulfite (Magnifite Process),
(2) Softwood unbleached sulfite (Mitscherlich Process),
(3) Hardwood neutral sulfite semi-chemical,
(4) Hardwood chemi-groundwood, and
(5) Softwood groundwood from chips given a mild sulfite-bisulfite pretreatment.

In newsprint or "ground wood" papers, almost all of the lignin in the original wood is present unchanged in the final paper. Such low cost papers containing significant amounts of lignin are especially useful in the present invention. However, it should be understood that other paper materials may also be used and that the lignin may be separately introduced or impregnated into the paper during or after its formation. This, of course, is a much less efficient method for producing the lignin containing paper sheet than by conducting a pulping operation which results in a paper containing a substantial or effective amount of lignin.

The color precursor which reacts with lignin to produce the visible reaction products may be any of a wide variety of compounds and compositions. The compounds of particular value include certain phenolics, aromatic bases, heterocyclics and inorganic materials.

Representative of the phenolics is phloroglucinol which rapidly forms an intense purple-red color with lignin in the presence of aqua HCl. Similarly 3-hydroxyphenyl ureau products an intense orange color.

Representative of the aromatic bases is aniline hydrochloride which rapidly forms an intense yellow with lignin in the presence of water. Similarly 4-aminophenylglycine hydrochloride yileds an orange-red color and N,N-dimethyl - p - phenylene-diamine hydrochloride yields an intense purple.

Representative of the heterocyclics is 3-aminopyridine which rapidly forms an orange color with lignin in the presence of aqua HCl. Similarly skatole forms a deep purple color, 3,4-dimethyl-5-pyrazolone an orange color, and 2-methylindole a deep purple.

Representative of the inorganics is cobalt thiocyanate which rapidly forms a deep blue with lignin bearing papers in the presence of moisture. The use of this compound in combination with one or more of the precursors cited above provides outstanding color formation upon reaction with lignin.

Many other compounds are known which react with lignin to provide a broad range of color possibilities. In some cases, however, the rate of color formation is too slow to be practically useful alone as a pressure sensitive color precursor. Many combinations of precursors are possible which provide a wide range of color possibilities from bright blues, greens, and yellows, intense reds and purples through "near blacks."

As noted above, the present invention lends itself to the formation of single or multiple sheet pressure sensitive record systems. Referring to FIGURE 1 of the drawdrawing, there is illustrated a pressure sensitive record system comprising a single element **10**. The element comprises a sheet of paper **11** containing lignin. As described above, the lignin may be left in paper manufactured from wood or other fibrous material, e.g., straw, not rags or cotton, by controlling the pulping process, or may be separately added to the cellulosic fibers. In the embodiment of FIGURE 1, color precursor is distributed throughout the paper in a passive, but pressure-activatable form, preferably in the form of encapsulated droplets **12** of the color precursor or the color precursor in a suitable solvent. By encapsulating the color precursor in a rupturable capsule, the system is rendered passive during normal handling, until the capsules are ruptured by pressure which releases the precursor into contact with lignin to produce the desired reaction. The paper base may also contain various whitening agents or other pigments or dyes, so that a good contrast is provided between the paper and the reaction products of the color precursor with lignin. Thus, the sheet may be tinted to give good contrast with the colored reaction products, e.g., it may be tinted pastel green for a red color former.

As shown in FIGURE 2, the record element **20** may comprise a color precursor **12** coated on the surface of a sheet of paper **13** which contains lignin. The color precursor may again be encapsulated or otherwise rendered passive under normal handling conditions, by being encapsulated or entrapped in a pressure-rupturable layer or film of binder material **15**. Upon application of writing or printing pressure to a surface of element **20** precursor **12** is exuded from film **15** and is adsorbed into the substrate where it reacts with the lignin present.

The materials of the present invention may also be utilized by producing highly efficient manifolding packs as illustrated in FIGURES 3 and 4.

The system illustrated in FIGURE 3 comprises an assembly **30** of two sheets **31** and **32**. The top sheet **31** is provided with a surface coating **33** which is at least partially pressure transferable and contains a color precursor of the type described above. The coating may comprise a solution or emulsion of a film forming material **34**, such as polyvinyl alcohol, nylon or other resinous material containing dispersed or encapsulated globules of a liquid or flowable precursor or a solution of a precursor **35**. Separate receiving sheet **32** is a paper sheet containing lignin. Pressure on selected portions of an exposed surface of assembly **30**, as by writing or typing, causes portions of coating **33** to be transferred to sheet **32** where the precursor reacts with lignin in the paper bringing about the desired color forming reaction. Entire film **33** need not be transferred it only being necessary that the film be ruptured or compressed so that a sufficient amount of the precursor **35** is exuded and transferred to sheet **32** for reaction with the lignin in that sheet.

Since in many cases pressure is applied to the upper surface of sheet **31** by means of a type bar, pen, pencil or other stylus which makes its own mark, it may not be necessary that sheet **31** contain lignin to form its own reaction marking. However, the top sheet could be of the type shown in FIGURE 1, impregnated with sufficient color precursor so that some of it would be transferred under pressure to an underlying receiving sheet, such as sheet **32** in FIGURE 3, and some would react in the body of the sheet itself.

A more complicated manifolding assembly **40** of three elements is illustrated in FIGURE 4. Top element **41** comprises a paper sheet **45** containing lignin and dispersed color precursor **46** in a passive condition. The lower surface of the paper sheet is coated with a layer **47** which is at least partially pressure transferable and also contains color precursor **48**. Element **42** which is in surface contact with element **41** comprises a paper sheet **45** containing lignin and a surface coating **47** which is pressure transferable and contains color precursor **48**. Element **43** comprises only a paper sheet containing lignin. If desired, films or coatings containing precursor may also be carried on the upper surfaces of sheets **32**, **33** and **34** in a passive condition. Under pressure, the precursor enters a color forming reaction with lignin, both in the carrying sheet and the adjacent sheet.

Upon the application of pressure to the upper element **41** it will be seen that a color-forming reaction is triggered in that sheet and in each of the underlying sheets. The reaction in sheet **41** is brought about by activation of the passive color precursor **46** within the paper sheet **41** itself. The color-forming reaction in the other sheets takes place by virtue of transfer of color precursor from the surface of a contacting sheet into the body of the adjacent lignin-containing paper sheet.

It will be obvious to those skilled in the art that various modifications may be made in the character and arrangement of the individual record elements and manifolding packs of the present invention.

EXAMPLE

A paper sheet containing lignin is prepared by the conventional chemi-ground wood process and contains about 20% residual lignin.

Micro-encapsulated cobalt thiocyanate is dispersed in a solution of polyvinyl alcohol, the solution is coated on the surface of the paper and dried. This forms a film of polyvinyl alcohol containing the microcapsules of precursor on the surface of the paper. Sufficient capsules are dispersed to amount to about 5% by weight of the paper.

Under writing pressure, the capsules rupture and the cobalt thiocyanate reacts with the residual lignin in the paper to form a dark blue color.

Micro-encapsulation of the color precursor may be achieved by a variety of methods. One suitable procedure is disclosed in following United States patent of the same assignee, in the name of Reyes and identified as U.S. Patent 3,173,878, issued on Mar. 16, 1965, and entitled Process of Making Microcapsules. The micro-encapsulated color precursor may be applied to the lignin bearing sheet by either an "on machine" or "off machine" operation. The "on machine" methods of application include beater addition, addition at the size press or addition at the calendar stacks, and constitute the preferred low-cost method of application.

The application of a dispersion of polystyrene micro capsules in an aqueous emulsion of polyvinyl acetate at the size press comprises the preferred "on machine" application for impregnating the lignin bearing sheet with the color precursor in passive form. (FIG. 1). Surface application of similar suspensions of micro-capsules can be achieved by "on machine" application at the calendar stacks or by an "off machine" application using conventional coating techniques such as reverse roll, air knife, etc., on the formed sheet. "Off machine" refers to a secondary operation on the finished sheet. It is usually more costly than "on machine" treatment because it evolves a second separate operation.

The lignin content of a sheet may be enhanced by similarly impregnating at the size press or surface coating with an aqueous suspension of purified lignin (5–10 microns in size). Cooperative Report of the U.S. Forests Products Laboratory, Paper Ind. 27, No. 11:1683–89 (February 1946).

Addition of passive color precursor at the paper ma-

chine to a newsprint furnish makes possible a very low cost pressure sensitive sheet.

The optimum concentration of lignin in the paper sheet ranges from a minimum of about 5% by weight of the base sheet to 35% or higher. Distribution of both color precursor and lignin throughout the sheet of course are of primary importance. Both reactants may also be surface coated and, if so, the concentration required will be less than if one or both is distributed throughout the base paper.

It will be obvious to those skilled in the art that certain modifications may be made in the composition and procedures described above without departing from the spirit or scope of the invention as expressed in the following claims.

What is claimed is:

1. A pressure sensitive record material comprising

a sheet of paper containing at least about five percent lignin, and

a color precursor substantially colorless which reacts with lignin under writing pressure to form visible reaction products, said reactant including at least one compound selected from the group consisting of phloroglucinol, 3-hydroxyphenyl urea, aniline hydrochloride, 4-aminophenylglycine hydrochloride, N,N-dimethyl - P - phenylene - diamine hydrochloride, 3 - aminopyridine, skatole, 3,4 - dimethyl-5-pyrazolone, 2-methylindole, and cobalt thiocyanate.

2. The pressure sensitive record material of claim 1 wherein said reactant is distributed substantially uniformly throughout the body of said sheet of paper.

3. The pressure sensitive record material of claim 2 wherein said reactant is contained in pressure rupturable capsules.

4. The pressure sensitive record material of claim 3 wherein said capsules are substantially uniformly distributed throughout the body of said sheet of paper.

5. The pressure sensitive record material of claim 1 wherein said reactant comprises cobalt thiocyanate.

6. The pressure sensitive record material of claim 5 wherein said reactant further comprises an additional organic precursor.

7. The pressure sensitive record material of claim 1 wherein said lignin is present in the body of said sheet of paper and said reactant is present in a coating on the surface of said sheet of paper.

8. The pressure sensitive record material of claim 1 wherein both said lignin and said reactant are present in a coating on the surface of said sheet of paper.

9. The pressure sensitive record material of claim 1 wherein said reactant is present in a coating on a substrate other than said sheet of paper and is transferable under writing pressure from to said sheet of paper to react with said lignin to form visible reaction products.

10. A manifolding assembly comprising a plurality of pressure sensitive record materials of the type defined in claim 1.

11. The pressure sensitive record material of claim 1 wherein the reactant is sufficient to amount to about five percent by weight of the paper.

12. The pressure sensitive record material of claim 1 wherein said reactant is phloroglucinol.

13. The pressure sensitive record material of claim 1 wherein said reactant is 3-hydroxyphenyl urea.

14. The pressure sensitive record material of claim 1 wherein said reactant is aniline hydrochloride.

15. The pressure sensitive record material of claim 1 wherein said reactant is 4-aminophenylglycine hydrochloride.

16. The pressure sensitive record material of claim 1 wherein said reactant is N,N-dimethyl-P-phenylene-diamine hydrochloride.

17. The pressure sensitive record material of claim 1 wherein said reactant is 3-aminopyridine.

18. The pressure sensitive record material of claim 1 wherein said reactant is skatole.

19. The pressure sensitive record material of claim 1 wherein said reactant is 3,4-dimethyl-5-pyrazolone.

20. The pressure sensitive record material of claim 1 wherein said reactant is 2-methylindole.

21. The pressure sensitive record material of claim 1 wherein said reactant is cobalt thiocyanate.

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U.S. Cl. X.R.

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