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3,732,141

PRESSURE-SENSITIVE RECORD MATERIAL

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24 Claims

ABSTRACT OF THE DISCLOSURE

Pressure-sensitive record material which involves the making of a vanadium-chelate print by pressure-release of droplets of a solution of an organic chelating agent in a hydrophobic liquid for color development by oil-insoluble vanadium salts. The print intensity, rate of print development, and resistance of the print to fading are optimized by addition to the print-developing coat of different combinations of calcium carbonate, silica gel and oil-soluble phenol-aldehyde resins.

This application is a continuation-in-part of U.S. application Ser. No. 94,170, filed Dec. 1, 1970, now abandoned which is itself a continuation-in-part of U.S. application Ser. No. 49,557, filed June 24, 1970, now abandoned.

PRIOR ART AND OBJECT OF THE INVENTION

The art of making pressure-sensitive record material by incorporating substantially colorless, liquid, encapsulated, chromogenic material in or on paper sheets for color development by an associated co-reactant in response to writing or printing pressures is well known. Green in U.S. Pats. Nos. 2,800,458 (now Re. 24,899) and 2,712,507 and Green and Schleicher in U.S. Pat. No. 2,800,457 teach the making of such record materials. As to the color-developing system, commercial development has centered on reactions involving colorless triphenyl-methane dye precursors such as Crystal Violet Lactone and co-reactant acidic materials such as acidic clays and oil-soluble phenol-aldehyde resins. Although many metal chelates, particularly of catechol derivatives, have long been known as highly colored, apparently black materials, suitable for use in water-based inks, the use of the metal-catechol reaction system as the in situ color generator for pressure-sensitive record material has not been widely practiced. Among the reasons that the metal-catechol reaction system has been largely avoided in the pressure-sensitive paper art is that, as far as is known, the reaction to make ink pigments has been taught exclusively as proceeding with both reactants in solution, either in hydrophobic or hydrophilic media, but commonly in water solution. The encapsulation of water and aqueous solutions is not commercially practical on a large scale in a competitive, low-priced market such as the record material market. The encapsulation of organic hydrophilic liquids is well known but is also generally avoided in commercial paper-coating practice because hydrophilic liquids are difficult to retain in microcapsules and because the coacervative encapsulation of hydrophilic liquids generally requires the use of hydrophobic liquid encapsulation vehicles that are expensive and troublesome to handle. Hydrophobic (oily) liquids are more readily retained in microcapsules and are encapsulated economically in an aqueous manufacturing vehicle. However, oil-soluble metal salts, suitable for reaction with oil-soluble chelating agents, are uncommon, expensive to make and use, generally more highly colored

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than the preferred water-soluble metal salts, and react too slowly with chelating agents in oil-solution to give a commercially useful record material. Thus the development of a system using hydrophobic liquid media with oil-soluble chelating agents and oil-insoluble metal salt particles for color-formation at the metal salt surface would be a significant advance in the pressure-sensitive record material art where the use of this reaction as a solution reaction has been largely avoided for the reasons cited.

Use was made of the gallic acid-ferric ion color-developing reaction by Green (U.S. Pat. No. 2,299,693) for a dried-emulsion-coated pressure-sensitive record material. Each of the two reactants was separately dissolved in glycerine which served as the hydrophilic reaction medium when the two solutions were brought together by writing pressure.

Kan et al. (U.S. Pat. No. 3,432,327) also disclose a similar system wherein a variety of metal ions and chelating agents are brought together for color-forming reaction in hydrophilic-media solution. The Kan system involves encapsulation by interfacial polymerization of either hydrophilic or hydrophobic liquids, but, when metal-chelate color generation is involved in the Kan system, at least one color reactant is always incorporated as an encapsulated hydrophilic-liquid solution in which the other color reactants provided are also soluble. Thus the problem of using metal-chelates in record material systems similar to successful commercial systems is a problem long in need of solving. The successful system wherein it would be advantageous to incorporate metal-chelate colorants may be defined as comprising paper base sheet material bearing in its body or on at least one of its surfaces at least two substantially colorless color-reactant materials at least one of which is dissolved in a hydrophobic liquid, which hydrophobic liquid is also provided in or on the base sheet material isolated from at least one of the color-forming reactants as the core material of microcapsules having walls of organic hydrophilic polymeric film material. The use of oil-insoluble metal salts and oil-soluble organic chelating agents, which may be generally viewed as catechol derivatives, in the just-defined system is an object of this invention. Further, the development of such a record material system that is still responsive after long shelf-life and which gives a rapidly-developed, distinctively-colored (preferably black), intense and fade-resistant print in response to imaging pressure is an object of this invention.

SUMMARY OF THE INVENTION

The objects of this invention have been successfully met. There is provided by this invention record sheet material comprising a base sheet of paper having coated on a surface thereof (1) microcapsules having walls of hydrophilic, organic, polymeric, film material such as gelatin which contain and isolate core material of droplets of a solution of an organic chelate-forming material in an organic hydrophobic liquid solvent which is capable of dissolving at least 3 percent, by weight, of said organic chelate-forming material (and preferably 5 percent to 10 percent or more); and (2) finely-divided particulate co-reactant material selected from the group consisting of oil-insoluble vanadium salts. The two color-forming reactants may be coated one on each of two sheets to give a transfer sheet and a receiving sheet or both on one sheet to give a self-contained copy-sheet. Such variations in distributions of color-forming reactants where one is dry and one is encapsulated as a solution are well known in the art and will also include such aforesaid variations as distribution in the body of a sheet as equivalent to distribution in a sheet coating. Examples of transfer sheets, self-

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contained sheets and receiving sheets will be given herein.

When vanadium salts are used herein reaction in mutual solution does not appear to be important. Oily solvents that dissolve the organic chelating agent may, but need not, dissolve appreciable amounts of the vanadium salts to give sufficient color formation for use in commercial record material. Therefore all vanadium salts that chelate with catechol derivatives are useful herein including for instance, ammonium vanadate, sodium vanadate, sodium orthovanadate, vanadyl acetate; vanadium acetylacetonate, and vanadyl acetylacetonate. Particularly useful are oil-insoluble (water-soluble) ammonium vanadate, sodium vanadate, and sodium orthovanadate. Oil-soluble vanadium salts such as vanadyl acetate, may also be used in conjunction with the eligible chelating agents but have the disadvantages of being more expensive, more highly-colored, and giving a slower solution reaction when used to develop color in the described record materials.

Hydrophobic liquid solvents eligible for use herein include amines such as 2-ethyl-1-aminoheptane, diisobutylamine, tributylamine; alcohols such as decanol and octanol; haloalkanes such as p-fluorotoluene; haloalcohols such as 2-methyl-3,3,4,4,5,5,6,6-octafluoro-2-hexanol; esters of inorganic acids such as tricresyl phosphate, tri-n-butyl phosphate; esters of organic acids such as di-n-butyl fumarate, di-n-octyl adipate, di-n-octyl phthalate, di-2-ethylhexyl phthalate also called dioctyl phthalate, and cottonseed oil; hydrocarbons such as monoisopropyl biphenyl; nitroalkanes such as 1-nitropropane; ketones such as 1-phenyl-2-propanone; and amides such as N,N-dimethyl oleic acid amide. All of these solvents dissolve sufficient chelating agent to react satisfactorily with vanadium salts. The list of solvents given here cannot hope to be complete. It should be noted that the listed solvents cover quite a variety of different chemical classes of oils. By empirical test, other eligible solvents can be readily found that dissolve at least 3 percent, by weight, of the selected chelating agent.

The use of vanadium chelates in ink formulations (particularly for black indelible inks) is well known and widespread. However, vanadium chelates are generally so-used in conjunction with other pigments and dyes because vanadium chelates fade badly from black to gray-green on aging, particularly when exposed to air and light. The virtue of vanadium chelates in indelible inks is the fact that some color (gray-green) remains in such a vanadium-chelate print even after harsh and extended exposure. This sort of fading, even if never complete, cannot be tolerated in a colorless, chromogenic system such as the instant system where additional black pigments and toners cannot be added without defeating the purpose of the designed colorless to colored chemical transition.

As can be readily seen, the commonly-experienced fading of vanadium chelates must be substantially eliminated before a commercial record material depending on vanadium-chelate colorants can be made. This problem, which is intimately linked to factors that also affect the print intensity and the speed with which a print develops, is solved in the instant invention by methods set out below.

It has been found that the addition to the receiving sheet slurry of particulate silica material tends to increase print intensity, the rate of print development, and the rate of print fade of a vanadium-chelate print made on a so-coated receiving sheet. Furthermore, the addition of finely divided, particulate calcium carbonate improves print intensity, substantially decreases the rate of print fade and does not substantially affect the rate of print development. The modification of a vanadium salt-coated receiving sheet by incorporation of both calcium carbonate and silica materials in the coating thereof gives a sheet that develops an intense print faster than a sheet coated with vanadium salt alone and also advantageously resists print fade better than the unmodified sheet. The enhancing effect of the silica material on print speed is

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particularly pronounced when the vanadium salt and the silica material are ground together, as in a ball mill, before they are mixed into the aqueous coating slurry.

A better solution to the problem of eliminating the print-fade of vanadium-chelate prints without impractically decreasing print intensity and rate of print formation resides in the incorporation of oil-soluble, polymeric phenol-aldehyde resin material in the vanadium salt coating. With or without calcium carbonate, the stability of vanadium-chelate prints are markedly improved in the presence of phenolic resins of the type described. As will be seen in the specific examples, the best balance of desired properties is achieved by development of prints between organic chelate-formers and vanadium salts on coated sheets also containing, in close juxtaposition, finely divided particles of silica gel and oil-soluble phenol-aldehyde resin material such as p-phenylphenol-formaldehyde or p-tert-butylphenol-formaldehyde resins. Eligible phenolic resins for this purpose are the same as those used to develop color in triphenylmethane dye precursors as taught and claimed in Canadian Pat. 768,039 of Robert E. Miller and Paul S. Phillips, Jr. However, it has been found that resoles, which found only limited use in the Miller-Phillips teaching, are particularly effective in stabilizing vanadium chelate prints and preventing their fading on exposure to light, air and moisture. The preferred phenolic resin for use herein is a p-tert-butylphenol-formaldehyde resin having a methylol content of about 16 percent. Eligible resoles for use herein are oil-soluble phenol-formaldehyde resins having a methylol content of 5-30 percent and preferably about 10-20 percent, wherein the phenol-formaldehyde resin is chiefly the reaction product of formaldehyde with a para-substituted phenol but which may also contain some phenolic units derived from phenols unsubstituted in the ortho and para positions. The inclusion of such para-unsubstituted phenolic units to modify the polymer chain may lead to some cross-linking (which is not particularly beneficial to the performance of the resins but which is not harmful if kept to a minimum) and to increased methylol content in the polymer composition. The preferred phenol-formaldehyde resin for use herein is a p-tert-butylphenol-formaldehyde resin which is about 50-60 percent tetramer or higher polymer, 20-30 percent trimer and 10-15 percent monomer-dimer, further characterized by having a methylol content of about 16 percent. Methylol-containing phenol-formaldehyde resins are well known in the art of resin making and molding and are designed to further polymerize on heating without the need for any additional cross-linking agent. The manufacture of such resins is not novel and does not constitute part of this invention inasmuch as there are many commercially available resins, made for other uses, that fulfill the requirements for use herein.

The mechanism by which such phenolic resins impart print stability to vanadium-chelate prints, even in the presence of silica gel which contributes enhanced print intensity and rate of development, is not understood. It seems unlikely that calcium carbonate and phenolic resins increase print stability by the same mechanism, but they both do this, and the described phenolic resins have been found particularly useful in this regard.

Among the eligible organic chelate-formers, for use in making the colored metal-chelate prints of this invention of particular use are derivatives of catechol: esters of gallic acid such as n-propyl gallate, n-butyl gallate, n-octyl gallate, 2-ethylhexyl gallate; alkyl catechols such as 4-tert-butylcatechol, 3,5-di-tert-butylcatechol, 4-(1,1,3,3-tetramethylbutyl)catechol, 3,6-diisopropylcatechol and nordihydroguaiaretic acid; 2,3-dihydroxynaphthalene; 2,3,4-trihydroxyacetophenone; pyrogallol; thiocatechols such as 2,2'-thiobis(p-cresol), 1,1'-thiobis(2-naphthol), 2,2'-thiobis(4,6-dichlorophenol), 2,2'-thiobis(6-tert-butyl-4-methylphenol); quercetin; and halocatechols such as tetrachlorocatechol and tetrabromocatechol. Many

organic compounds, other than those listed above, are known to give usefully-colored chelates with iron salts and vanadium salts. One schooled in the art could readily choose other useful organic chelate-formers.

An additional and unexpected advantage in the manufacture of the record materials of this invention is that the color-producing reactions used herein proceed satisfactorily in the presence of commonly used printing ink vehicles which contain polar non-volatile liquids such as glycols and esters. Color development in colorless chromogenic dye precursor materials such as Crystal Violet Lactone that generate color as a result of an acid-base reaction is inhibited by such polar non-volatile vehicles. When solutions of the organic chelate-formers of this invention are encapsulated, the capsules may be suspended in printing-ink vehicles, including polar, non-volatile printing-ink vehicles, and printed on a paper surface by means of a printing press to make a pressure-sensitive transfer sheet. Capsules have previously been printed onto paper sheets but, as far as is known, such practices have always been limited to the use of special uneconomical printing vehicles or printing processes when the contents of the capsules are droplets of colorless chromogenic materials. The use of common non-volatile, polar, printing-ink vehicles and processes for the printing of capsules on paper to make a record material transfer sheet has been limited to capsules having already-colored contents such as carbon-black or other pigments.

As a practical matter, when coacervation in an aqueous vehicle is used to encapsulate the hydrophobic liquid solution of the organic chelating agent, said agent should be substantially water insoluble, preferably less than 1 percent soluble.

It should be noted that the so-called thiocatechols, mentioned above are all o,o'-thiobisphenols such that the thio-substituent is shared by the two rings and each of the two rings may be viewed as a thiocatechol derivative. These "double" thiocatechol derivatives do not give as intense prints as the alkyl gallates but are useful in practicing the instant invention inasmuch as they generally give more stable vanadium-chelate colors that contribute to print-fade resistance.

With 2-ethylhexyl gallate and ammonium vanadate (the preferred chelate-forming reactants), the preferred solvent is a 4:1 mixture (parts by weight) of di-2-ethylhexyl phthalate and tri-n-butyl phosphate. In general, a solvent to be an effective vehicle in this system should be a hydrophobic liquid capable of dissolving sufficient organic chelate forming material to make a solution of at least 3 percent, by weight, and a like amount of iron salt, if iron salts are used. In the record sheet material of this invention, solvents and organic chelate-formers have been chosen such that the solvent is capable of making a 10 percent, by weight, solution of the chelating agent. Any eligible solvent which is sufficiently strong to still dissolve sufficient quantities of the chelating agent after dilution with liquid aliphatic hydrocarbons may be so diluted. When vanadium salts are used, appreciable solubility of the vanadium salt in the chosen solvent is not required and oil-insoluble vanadium salts are preferred.

Following are a number of examples of coating slurries and coated record material sheets that will serve to illustrate embodiments of this invention. In the examples, unless otherwise specified, all parts and solution concentrations are parts by weight and weight percents.

Transfer sheets

A series of capsule-bearing transfer sheets (3 pounds of capsules per ream of 500 sheets, measuring 25 x 38 inches) was prepared by coating the following general aqueous slurry formulation on base sheets of bond paper with a No. 18 Mayer coating rod:

	Parts, wet	Parts, dry
Capsules	220	40
Alpha-cellulose fibers	15	15
Starch binder (aqueous)	20	4

A little additional water may be added if needed to give a good coating consistency.

The capsules were made according to the procedure shown in the following section with various internal phases. The different internal phases which gave the different coated sheets (called CB (coated-back) sheets) were as follows:

Internal phase of capsules (10 percent solutions)

15 CB sheet designation:	
A ---	EHG in DOA.
B ---	EHG in TBP.
C ---	EHG in 1:1 DOA-TBP.
D ---	EHG in di-n-butylphthalate.
20 E ---	EHG in 1-phenyl-2-propanone.
F ---	EHG in decanol.
G ---	Propyl gallate in 1:1 TCP-TBP.
H ---	2,3-dihydroxynaphthalene in 1:1 TCP-TBP.
I ---	2,3,4-trihydroxyacetophenone in TBP.
25 J ---	3,6-diisopropylcatechol in TBP.
K ---	Nordihydroguaiaretic acid in TBP.
L ---	1:1 EHG-2,2'-thiobis(4,6-dichlorophenol) in 1:1 TBP-DOA.

(EHG is 2-ethylhexyl gallate. DOA is di-2-ethylhexyl adipate which is commonly called dioctyl adipate. TBP is tri-n-butyl phosphate. TCP is tri-cresyl phosphate.)

Liquid-containing capsules

An aqueous emulsion having oil droplets of 2 to 3 microns diameter was prepared by stirring in a Waring Blendor the following materials at 55 degrees centigrade. (All water used herein was deionized water.)

200 grams of the selected internal phase solution
200 grams of 10 percent aqueous gelatin
50 grams of water.

With continual stirring and maintenance of the temperature at 55 degrees centigrade, the pH of the stirred emulsion was adjusted to 6.5, and the emulsion was treated with 133 grams of 10 percent aqueous gum arabic solution and then diluted with 700 grams of water. The stirred mixture was then treated with 12 grams of 5 percent aqueous poly(methylvinylethermaleic anhydride) copolymer solution, added dropwise. About 15 milliliters of acetic acid were added to adjust the pH of the mixture to 4.5. With continued stirring, the mixture was cooled to 15 degrees centigrade, treated with 10 milliliters of 25 percent aqueous glutaraldehyde and allowed to stir at room temperature for 48 hours. The completed capsule units were used as a suspension in the manufacturing vehicle without isolation.

Receiving sheets with Vanadium salt

A series of CF coating slurries were prepared by mixing, in an attritor, the various additives shown below with 1.5 parts of ammonium vanadate, 2 parts of starch, 18 parts of latex and 150 parts of water:

CF sheet designation:	Parts of additives
CF-2	80 "Syloid-72."
CF-3	80 CaCO ₃ .
CF-4	40 "Syloid-75," 40 CaCO ₃ .
CF-5	3 "Syloid-72," 36 CaCO ₃ , 8 para-phenylphenol-formaldehyde resin.
CF-6	76 "Syloid-72," 4 para-tert-butylphenol formaldehyde resin, 2 glycerin.

("Syloid" is the trademark name for a family of synthetic, micron-sized, amorphous silica gels, sold by the

Davison Chemical Division of W. R. Grace and Company, Baltimore, Md. 21203. "Syloid-72" and "Syloid-

sheet to decrease the print intensity and increase the print stability (compared to silica-containing sheets).

	CF-2	CF-3	CF-4	CF-5	CF-6
CB-A-----				56, 49, 51, 56	49, 46, 56, 60
CB-B-----	54, 37, 55, 53	97, 81, 58, 61	69, 48, 53, 65	63, 46, 44, 54	52, 38, 46, 51
CB-C-----					49, 44, 53, 56
CB-D-----					
CB-E-----					
CB-F-----					
CB-G-----					52, 42, 48, 50
CB-H-----					55, 43, 51, 51
CB-I-----					40, 27, 40, 47
CB-J-----					37, 27, 64, 52
CB-K-----					60, 41, 49, 42
CB-L-----					56, 46, 54, 55

75" are nearly neutral, highly oil absorbent silica gels, grade 72 having an average particle size of about 4 microns and grade 75 about 2.6 microns. The latex used herein was a carboxylated 60:40 styrene-butadiene latex such as "Dow 620" (trademark) sold by the Dow Chemical Company, Midland, Mich. Substitution of different binder materials was not critical. The above styrene-butadiene latex as well as acrylic latexes, polyvinyl acetate latexes, starch solutions and polyvinyl alcohol solutions were all found to work satisfactorily either alone or mixed with another binder material.

Coating of the above CF coating slurries was carried out as described for CF-1 to give CF-2 through CF-6. Results of tests of these sheets in combination with a series of CB sheets is shown below.

Record material performance

Record sheet material couplets were made for testing, using the above CB (transfer) sheets and CF (receiving) sheets, superposed one against the other with their coated surfaces together in the middle of the couplet. The CB coating acted as a transfer surface when the uncoated surface of the CB sheet was typed on to break the CB coating capsules in an image pattern and release the liquid contents of the capsules onto the CF coating of the receiving sheet for color development. Transfer prints made on the receiving sheets were tested for print intensity by use of a reflectance spectrophotometer (opacimeter). Typewriter intensity indexes (which are 100 times the ratios of print reflectances versus background reflectances) are reported here for the most interesting CB-CF combinations. A typewriter intensity index (TI) of 100 indicates no detectable print and the lower numbers indicate more intense prints, showing greater contrast with the background. Most of the values reported here are of commercial quality although some CB-CF combinations are reported here to show the effect of various additives even though the CB-CF combination may be of less than commercial quality in some respects. Generally, a typewriter intensity index of less than 60, for a black print, indicates a print which is sufficiently intense to be esthetically pleasing and readily read by the human eye.

The four figures reported in the accompanying table for the various CB-CF combinations are, in the order shown: the TI taken immediately after the print is made, the TI taken 20 minutes later, the TI taken after 50 hours exposure to sunlight through window glass, and the TI taken after one week exposure to room light (night time, dark; daytime, fluorescent light plus indirect sunlight).

Thus for any given CB-CF combination a comparison of the first two numbers is an indication of the speed of the color development. The closer the first two numbers are to each other in value, the greater the amount of potential color which actually developed immediately.

The third and fourth numbers reported for each CB-CF combination are a measure of the print stability or fade resistance of each print. If the third and fourth numbers closely approximate the second number, the print may be judged to not fade under the test conditions.

Comparison of CF-3, CF-4 and CF-5 with CF-2 and CF-6 show the inclusion of calcium carbonate in the CF

Comparison of CF-2 and CF-4 with CF-3 shows the advantage of including silica gel in the CF formulation. In general CF sheets containing finely-divided, amorphous silica gel material have been found to give faster print-development and more intense prints than those omitting silica gel from their formulations. However, the greatest advantage has been found when said silica gel is nearly neutral (5 percent slurry in water, pH 6.6 to 7.6), and shows an oil absorption capacity of 150 pounds or more per 100 pounds of silica gel.

The addition of an oil-soluble phenol-aldehyde resin to a CF sheet already containing silica gel gives a slight print intensity improvement as seen by comparing CF-4 with CF-5. In fact, oil-soluble phenol-aldehyde resins are so effective in this regard that the use of calcium carbonate may be regarded as optional: CF-6, an excellent vanadium CF sheet, contains no calcium carbonate and gives satisfactorily intense and stable prints. Satisfactory CF sheets, not as good as CF-6 for instance, were made by omitting both the calcium carbonate and the silica gel, with only p-phenylphenol-formaldehyde resin present to aid print development and stability. A small amount of glycerin was generally added to phenol-formaldehyde-resin-containing CF formulation to prevent yellowing of the sheet.

The shelf-life of the coated sheets of this invention has been found to be remarkably good. For instance, CB-A and CB-C sheets have been found to perform satisfactorily after storage for three weeks under the harsh conditions of 90 degrees Fahrenheit—90 percent relative humidity. In general, the CF sheets of this invention give better prints after aging than when they are freshly made—that is more intense prints of equal stability develop more rapidly after aging of the CF sheets.

An alternative method of CB sheet manufacture consists of isolating on the paper surface the organic chelating agent hydrophobic solution droplets in a continuous film which is the dried residue of an aqueous emulsion of the hydrophobic droplets and a polymeric film-forming material such as gelatin or gelatin-gum arabic. In general the dried emulsion film does not perform as well as individual microcapsules.

Self-contained record sheet

When bond sheets were coated with one of the previously shown CB coating slurry formulations and then after drying, given a second or over-coat of one of the shown CF coating slurries, a self-contained sheet resulted that responded to writing pressure, without other agency, by yielding a distinctively-colored mark, in the pressure pattern. A particularly useful combination of coatings for preparation of self-contained sheets was the CF-6 slurry coated over a CB-B coat. It was found that similar results were also obtained by reversing the coating order and coating a CB slurry over a CF coat.

Preferred record sheet material

The preferred CB transfer sheet was made as set out above with capsules having an internal phase of a 10 percent solution of 2-ethylhexyl gallate in a 4:1 mixture of di-octyl phthalate and tri-n-butyl phosphate. The preferred

CF receiving sheet was made as set out above with the following amounts of materials: 1 part of ammonium vanadate, 1 part of starch binder, 14 parts of latex binder, 123 parts of water, 2 parts of sodium silicate, 10 parts of "Syloid-72,55 69 parts of calcium carbonate, and 3 parts of p-tert-butylphenol-formaldehyde resin having a meth-
 ylol content of 16 percent.

What is claimed is:

1. Record material comprising base sheet material having coated thereon at least two color-forming reactants and associated binder material, wherein a first one of said color-forming reactants is an organic chelate-forming material which is dissolved in a hydrophobic liquid and maintained on said base sheet material as contained and isolated droplets in solid, organic, pressure-rupturable, hydrophilic, polymeric film material, wherein a second one of said color-forming reactants is a finely-divided, oil-insoluble vanadium salt, and wherein no hydrophilic liquid is provided on said record material in addition to said hydrophobic liquid.

2. The record material of claim 1 wherein said base sheet material comprises two base sheets, a first base sheet having coated thereon the first one of said color-forming reactants and a second base sheet having coated thereon the second one of said color-forming reactants, said two base sheets being superposed one against the other with their coated surfaces together.

3. The record material of claim 1 wherein the hydrophobic liquid used to dissolve the organic chelate-forming material is an ester.

4. The record material of claim 3 wherein the ester is selected from the group consisting of tricresyl phosphate, tri-n-butyl phosphate, di-octyl phthalate and di-octyl adipate.

5. The record material of claim 1 wherein the organic chelate-forming material is a derivative of catechol.

6. The record material of claim 5 wherein the catechol derivative is a gallate ester.

7. The record material of claim 5 wherein the vanadium salt is selected from the group consisting of ammonium vanadate, sodium vanadate, sodium orthovanadate.

8. The record material of claim 5 wherein the catechol derivative is selected from the group consisting of 2-ethylhexyl gallate, nordihydroguaiaretic acid, 2,3,4-trihydroxyacetophenone, alkyl catechol, 2,3-dihydroxynaphthalene, and 2,2'-thiobis(4,6-dichlorophenol).

9. The record material of claim 8 wherein the vanadium salt is ammonium vanadate.

10. Record material comprising base sheet material having coated thereon at least two color-forming reactants and associated binder material, wherein a first one of said color-forming reactant is an organic chelate-forming material which is dissolved in a hydrophobic liquid and maintained on said base sheet material as contained and isolated droplets in solid, organic, hydrophilic, pressure-rupturable, polymeric film material, wherein a second one of said color-forming reactants is a finely-divided vanadium salt, and wherein said vanadium salt is intimately mixed with an anti-fade agent constituting a polymeric, oil-soluble, phenol-aldehyde resin material, and wherein no hydrophilic liquid is provided on said record material in addition to said hydrophobic liquid.

11. The record material of claim 10 wherein said vanadium salt is selected from the group consisting of ammonium vanadate, sodium vanadate, sodium orthovanadate, vanadyl acetate, vanadium acetylacetonate and vanadyl acetylacetonate.

12. The record material of claim 10 wherein the hydrophobic liquid used to dissolve the organic chelate-forming material is an ester.

13. The record material of claim 12 wherein the ester is selected from the group consisting of tricresyl phosphate, tri-n-butyl phosphate, di-octyl phthalate and di-octyl adipate.

14. The record material of claim 10 wherein the organic chelate-forming material is a derivative of catechol.

15. The record material of claim 14 wherein the catechol derivative is a gallate ester.

16. The record material of claim 14 wherein the catechol derivative is selected from the group consisting of 2-ethylhexyl gallate, nordihydroguaiaretic acid, 2,3,4-trihydroxyacetophenone, alkyl catechol, 2,3-dihydroxynaphthalene, and 2,2'-thiobis(4,6-dichlorophenol).

17. The record material of claim 16 wherein the vanadium salt is selected from the group consisting of ammonium vanadate, sodium vanadate and sodium orthovanadate.

18. The record sheet material of claim 10 wherein said vanadium salt and said phenolaldehyde resin material are intimately mixed with fine particles of silica gel.

19. The record material of claim 18 wherein the resin material has a methylol content of 5 percent to 9 percent.

20. The record material of claim 18 wherein the vanadium salt, silica gel, and resin material are intimately mixed with finely divided particles of calcium carbonate.

21. The record material of claim 19 wherein the resin material is a phenol-formaldehyde resin having phenolic units derived chiefly from p-tert-butylphenol.

22. The record material of claim 21 wherein the vanadium salt is selected from the group consisting of ammonium vanadate, sodium vanadate, and sodium orthovanadate.

23. The record material of claim 18 wherein the silica gel is a highly oil-absorbent, amorphous silica gel of nearly neutral pH.

24. The record material of claim 23 wherein the vanadium salt is selected from the group consisting of ammonium vanadate, sodium vanadate, and sodium orthovanadate.

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