

[54] **ELECTROSENSITIVE RECORDING MEDIA**

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[51] **Int. Cl.²** **B44D 1/02; B32B 3/02**

[58] **Field of Search**..... **346/74 SB; 117/216, 215, 117/65.2, 60, 217; 428/195, 212, 409, 538; 427/58, 121, 126, 299, 122**

[56] **References Cited**

UNITED STATES PATENTS

2,876,060	3/1959	Chambers	346/74 SB
3,113,511	12/1963	Dalton	117/216
3,220,345	11/1965	Kline et al.	117/216
3,263,604	8/1966	Dalton	117/216
3,368,918	2/1968	Miro et al.	346/74 SB
3,434,878	3/1969	Reis	117/215
3,511,700	5/1970	Miro	117/215
3,789,425	1/1974	Matsushima	346/74 SB

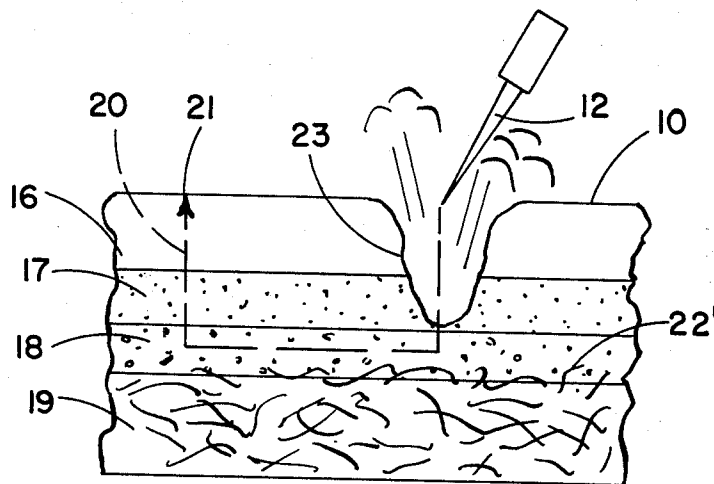
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[57] **ABSTRACT**

Particular embodiments illustrate improved spark recording media, including electroresistive material, adapted to develop informational indicia and/or to record the same, upon being subjected to an electrical discharge with a "burn-off fragrance" additive therefor adapted to ameliorate "burning" and attendant image degradation and to dissipate objectionable odors associated with such recording, especially after a spark discharge thereon; this additive particularly comprising an odor-affecting agent incorporated in a subsurface layer of the medium, and/or comprising fragrance material adapted to vaporize, but preferably not burn, at the temperatures developed during such recording, as well as during associated operations and handling.

More particularly, an additive of the foregoing type comprising fragrance oils, especially the volatile, non-burning, non-tar-producing oils; and more especially "candle fragrances" or "flame fragrance" oils of the type known as adapted for candle fragrances which vaporize in the burning of a candle, yet do not wick-up or burn (combust) substantially under normal use; such additives also optionally including other non-perfume substances which are non-combustible in the discharge environment and/or additives especially adapted to promote spark recording.

15 Claims, 8 Drawing Figures



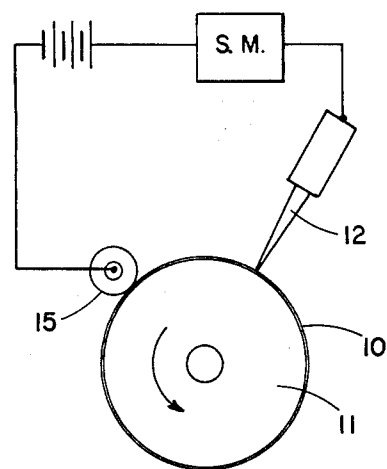
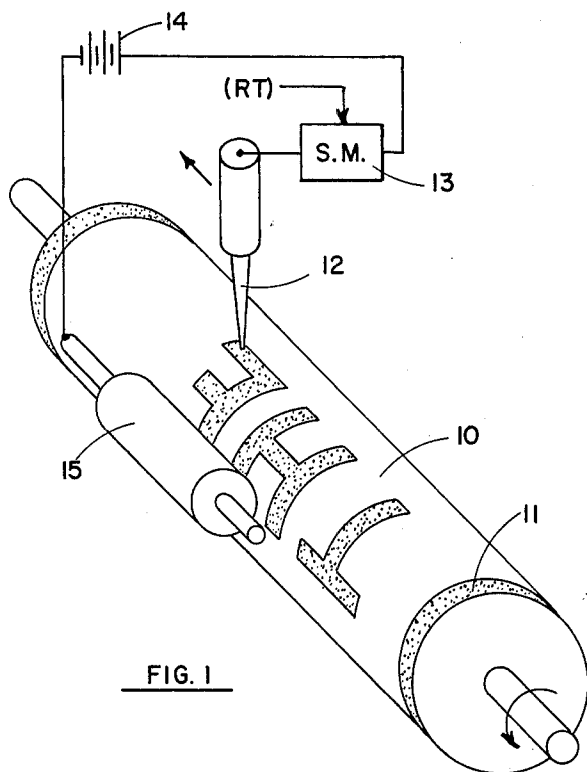


FIG. 2

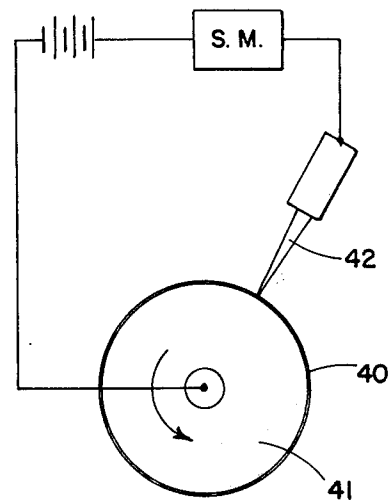
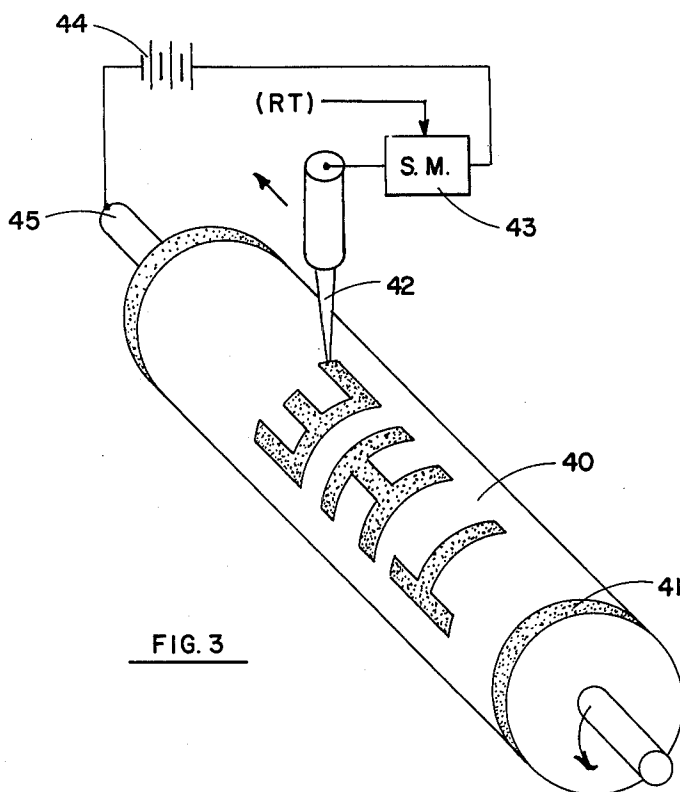


FIG. 4

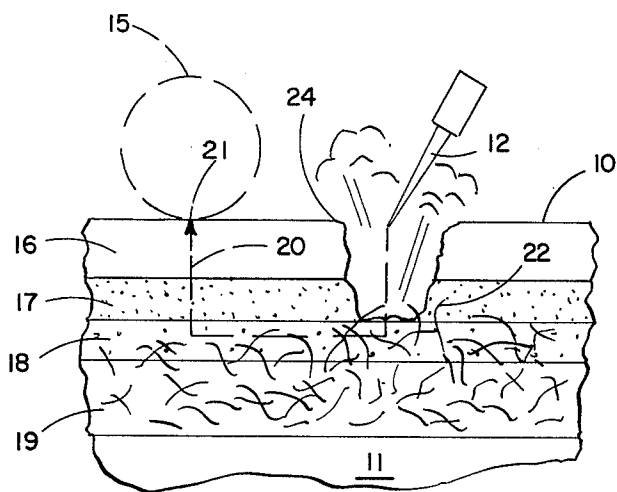


FIG. 5

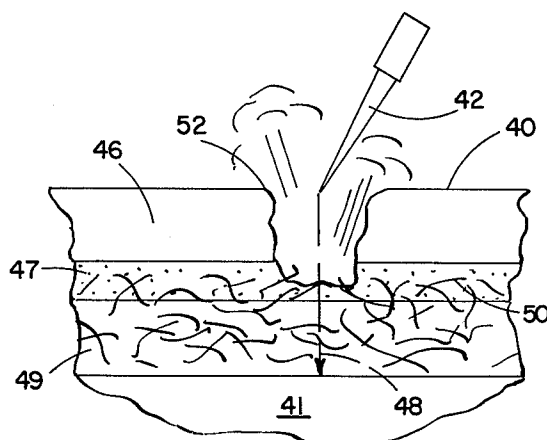


FIG. 6

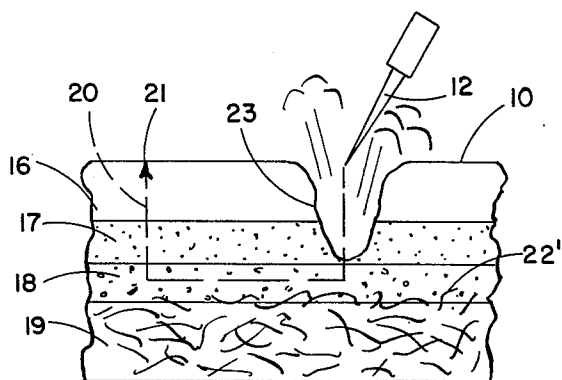


FIG. 7

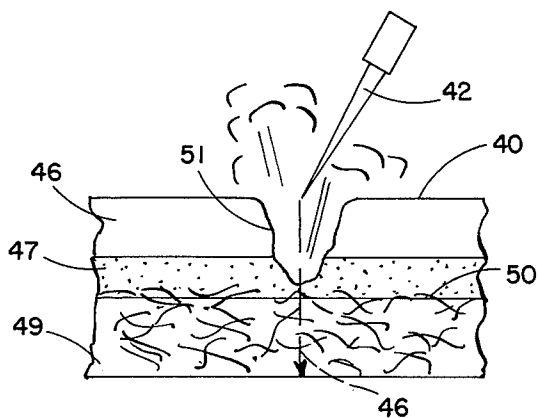


FIG. 8

ELECTROSENSITIVE RECORDING MEDIA

BACKGROUND

1. Field of the Invention

This invention is in the field of electrical recording media for various data, message, and graphic imaging devices. More specifically, it concerns an improvement in the preparation of electroresistive elements, commonly known as "spark-recording", "burn-off" or "electrosensitive recording" papers, films and foils, whereby obnoxious odors generated during the recording process are significantly reduced, masked, or modified. In a particular embodiment of this invention, image clarity is also improved.

2. Description of the Prior Art

Spark recording papers were first introduced some 30 years ago by Western Union, under the tradename "Teledeltos". Several other manufacturers have since developed similar products, these consisting of a white, or light-colored, layer coated over a black, or dark-colored, conductive interlayer on a conductive paper or film support. A modulated electrical signal passing through a stylus or other spark discharge device in contact with the surface of the record blank causes the light-colored coating to be selectively removed in prescribed "image areas" responsive to signal variations thereby producing a recorded image by revealing the black interlayer.

Where a plain paper, film, or other insulating base is used, the record blank is said to be "surface-conductive" as the current path enters and exits through the surface coating. Where a conductive paper, foil, or other low-resistance base is used, the record blank is said to be "through-conductive" as the current path travels entirely through the sheet. "Surface-conductive" papers are also called "front grounding" while "through-conductive" papers are said to be "back grounding".

The preparation of "surface" and "through-conductive" electrosensitive recording papers is well known to the art and reference is made to the work of Davis and Kingston in U.S. Pat. No. 3,514,325; to Miro in U.S. Pat. No. 3,511,700; to Dalton in U.S. Pat. No. 2,644,044, U.S. Pat. No. 2,554,017, and U.S. Pat. No. 2,555,321; and to Cooley et al. in U.S. Pat. No. 2,638,422.

The process by which the white surface coating is removed has been described variously as combustion, deflagration, explosion, or metal oxide reduction depending upon the composition of the cooperating layers. However, all prior art electroresistive papers and films generate smoke, odor, and debris, the amount varying with signal intensity and sheet construction.

Attempts to eliminate these undesirable by-products have in the past been focused largely upon the recording equipment rather than the record medium (blank). Various air filtration systems have been devised to capture the vapors generated during spark recording and to filter out the combustion products and debris, using charcoal granules or other absorbent substances.

Air filtration is effective in preventing debris from building up in the sensitive electronic circuitry usually associated with facsimile or data recording instruments, but it is not a complete solution. The need to replace a filter cartridge periodically places an additional maintenance burden on the service group responsible for the machine. Meanwhile, filtration efficiency grad-

ually degrades as the build-up of absorbate cuts down on the amount of air drawn through the filter bed.

Another reason air filtering devices have not proven completely acceptable in spark recording machines is that they do not effectively eliminate odor; yet it is the odor which an operator finds most offensive. The operator can hardly detect the amount of debris generated during a particular transmission, but he can immediately sense the offensive fumes emanating from the machine.

A further consideration is that smoke and debris emitted by a record sheet are no longer produced when the recording process is terminated. Odor can, however, be detected for several minutes afterward.

OBJECT AND SUMMARY OF THE INVENTION

A general object of this invention is to meet at least some of the foregoing and related problems. Another object of this invention is to reduce, mask, modify or eliminate the unpleasant smell associated with dry, electrosensitive recording papers at the instant spark recording takes place.

Another object of this invention is to reduce or eliminate the odor given off by the record sheet itself for a period of time after the copy has been produced on a spark-recording device.

A further object of this invention is to improve the resolution and clarity of images recorded on "surface-" and "through-conductive" papers or fibrous supports.

A more particular object is to eliminate the combustion of fibrous materials associated with such media; especially by spark deodorizing additives provided in or on one or several of the subsurface layers of such a medium. A related object is to provide additives and/or techniques adapted to eliminate, remove or redirect such fibrous material as may protrude into the recording region, especially where such media comprise a fibrous base including a number of combustible fibers apt to penetrate a super-coating; a further related object is to provide such a base with a protective coating so as to prevent the projection of such fibers thereabove; and/or to calender such a fibrous base sheet, or otherwise press it, for this purpose. Another related object is to apply such fragrances to a smooth, continuous base contact surface or superpose recording material

These and other objects will become apparent from the description that follows of preferred embodiments, along with consideration of the accompanying drawings.

In accordance with the method and means of the present invention, such media are improved to reduce the effect of burning and resultant image degradation and objectionable odors. Such odors, especially those persisting after the discharge, are reduced especially well by removing fibrous or cellulosic material from the discharge region, or by inhibiting the combustion thereof and/or by the addition of volatile fragrance material adapted to vaporize, but not burn, at the temperatures developed at these regions during recording.

These objects and features are preferably implemented by removing cellulosic (fiber) materials from contemplated discharge region. For media comprising a fibrous base with recording material coated thereon, this may be accomplished by compressing and/or coating fibres so they do not project up into these recording layers; this being effected, for instance, by a calendering, or like compressing, of the fibers into the base and/or by a smoothing, coating, or "sizing" of the base sur-

face contacting these layers whereby such burning and objectionable persisting odors may be prevented or ameliorated, and also whereby the resolution and clarity of the recorded image is enhanced, especially for surface conductivity applications.

The foregoing general object may be implemented by coating or otherwise conditioning fibrous portions of such a medium, as used in "front-grounded" recording to minimize uptake of material therein which increases the electrical conductivity thereof.

This general object may be implemented where the recording medium comprises a fibrous substrate base with recording material coated thereon, by rendering the coated surface of this base smooth and/or relatively compact so that individual fibers projecting therefrom are minimized.

The features and objects mentioned may especially be implemented by adding volatile fragrances to one or more of the subsurface layers of a multi-layer recording medium, to be volatilized during the contemplated spark recording; especially where such fragrances comprise non-burning, non-tarry materials volatile at the contemplated recording temperatures generated by the spark discharge; and more particularly where such fragrances comprise "flame fragrance" oils and the like selected for wax candle fragrances and adapted to vaporize, but not burn, at such temperatures; and most especially where such candle fragrances comprise oils which vaporize readily rather than burn.

The foregoing media are also adapted to comprise a substrate base rendered as a non-fibrous, smooth material, such as a smooth plastic "front-grounded" film or a conductive metallic "back-grounded" film.

In particular embodiments of such improved media, certain specific "burn-off fragrances", or like odor-masking agents are incorporated in the dark-colored coatings lying beneath the surface layer so as to mask, modify, disguise or otherwise improve the odor generated. In one embodiment concerning a paper (fibrous) substance, the surface is finished, sized, or calendered for maximum smoothness prior to application of the various coatings to minimize the amount of fiber that projects into the coated layers, it being found that these individual projecting fibers are responsible for much odor persistence.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a top perspective view and FIG. 2 a schematic side view of a spark recording device of a type known in the art for producing an image on a "surface-conductive" sheet.

FIG. 3 is a perspective view and FIG. 4 a schematic side view of a spark recording device producing an image on a "through-conductive" sheet.

FIGS. 5 and 6 are enlarged cross-sectional, merely theoretical and idealized views of conventional "surface-" and "through-conductive" recording papers, respectively.

FIGS. 7 and 8 are enlarged cross-sectional views of surface and through-conductive recording papers embodying and illustrating what are considered to be effects of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIGS. 1, 2 and 5, there is shown a "surface-conductive" (or front conductive) record sheet 10 carried on a rotating drum 11. A stylus needle 12 is in

light contact with the record sheet and the needle 12 is advanced axially, in a scanning mode in synchronization with the speed of drum rotation, in any manner known in the facsimile arts.

Record 10 is conventional and comprises a fibrous paper base support 19 of relatively high resistivity (volumetric and surface), a dark-colored conductive "ground coat" 18 on base 19, a "dark" coated layer 17 on coat 18 and a light-colored surface layer 16 (both latter layers being of intermediate resistance so as to "pass" expected current signals). Typical thicknesses would be: about 2.8 mils for the paper base support 19; about 0.50 mils for the conductive ground coat 18; about 0.75 mils for the dark-colored intermediate layer 17; and about 0.30 mils for the light-colored surface layer 16.

The electrical potential (and/or current) at the needle electrode 12 is determined by the signal modulator 13 which regulates the flow of current from the power supply 14 so that image areas of an original document or other subject matter at a remote transmitter (RT) produce a signal which causes current to flow from the needle electrode 12 through the record blank 10, thereby selectively removing, by spark discharge, "image portions" of the light-colored surface coating 16 and exposing the underlying dark-colored intermediate layer 17 and base 18 coatings to produce dark areas corresponding to the original image or subject. The current flow path 20 is from the stylus needle 12 through layers 16, 17 across the highly-conductive base coating 18 proceeding toward "return electrode" (roller) 15, to emerge through layers 17, 16 as indicated in FIG. 5 at the front roller electrode 15 (or other broad-area electrode) in rolling, or sliding, contact with the sheet surface. No current flows into the paper base 19 because it is non-conductive having a surface resistivity greater than 1×10^6 ohms per square cm. when measured at standard conditions of 73°F and 50 percent RH (relative humidity). Base 19 may typically exhibit pulp fibers 22 which project up into layer 18, and possibly layer 17.

Owing to the broad surface of the roller electrode 15, the electrical energy dissipated over a large area and not concentrated at any one point, will produce no mark as current flow exits from the surface of the record blank (at exit focus 21).

Referring to FIGS. 3, 4 and 6, there is shown a "through-conductive" record sheet 40 carried on a rotating drum 41. A stylus needle 42 is in light contact with the record sheet 40 and the needle 42 is advanced axially in a scanning mode in synchronization with the speed of drum rotation in any manner well-known in the facsimile scanning arts. Record 40 is conventional and comprises a conductive support base 49, a dark-colored layer 47 and a light-colored surface layer 46 (both layers, like 17, 16 above, being of intermediate resistance and, typically, about 0.75 mils and 0.30 mils thick, respectively).

The electrical potential at the needle electrode 42 is determined by the signal modulator 43 which regulates the flow of current from the power supply 44 so that the image areas of an original document or other subject matter at a remote transmitter (RT) produce a signal which causes current to flow from the needle electrode 42 through the record blank 40 thereby blasting away the light-colored surface coating 46 and exposing dark-colored intermediate layer 47 to produce dark areas corresponding to the original image subject.

The current flow path 48 is from the surface of the record blank 40 through the conductive base 49 to the drum surface 41 which is in contact with the back of the record sheet 40. The conductive base 49 can be a metallic foil element or a carbon-filled paper or fibrous base provided its surface resistivity is less than 1×10^4 ohms per square cm. Carbon-filled base papers for through-conductive recording are typically 3.0 mils thick prior to coating. As with base 19, base 49 may exhibit projecting pulp fibers 50.

In comparing FIG. 5 against FIG. 6, it is apparent that the current path 20 of the "surface-conductive" sheet 10 is less apt to encounter pulp fibers 22 from the fibrous paper base 19 than the current path 48 in the "through-conductive" sheet 40 where electrical energy passes directly through the fibrous base 49 is apt to encounter projected fibers 50.

Because individual fibers 50 (FIGS. 6, 8) are directly in the path of current flow, they are more likely to be ignited and to smolder, thereby increasing the amount of smoke, odor, and debris generated in the process of recording. Also, it is believed that the smoldering fibers are the major reason that the odor continues to persist, emanating from the record blank for several minutes after the recording process has ceased.

The tendency of pulp fibers 50 to ignite, smolder and smoke is further increased by conductive filler materials used in the paper base 49. Carbon-filled papers are usually employed so that each fiber is surrounded by sub-micron particles of activated charcoal or carbon black, a highly combustible material.

The non-conductive base 19 of FIG. 3 is not directly in the path of current flow 20 and, therefore, the only fibers 22 (FIGS. 5, 7) which might be ignited are those loose surface fibers 22 that may penetrate the base 18 and intermediate 17 layers.

According to a feature hereof, I have discovered that one can improve recording by adding certain fragrant materials, particularly candle fragrance oils of various scents, to either or both of the base and intermediate layers of an electroresistive recording paper. This yields good results, presumably because the odor generated is successfully masked, modified, or disguised so that it is no longer unpleasant and/or as noticeable.

I have further discovered that odor and fume generation is reduced by the practice of providing a highly calendered base sheet having a minimum of surface fibers available for penetration into the conductive base, intermediate and top coat layers. These features will be further treated in Examples below, but first a theory of their operation will be treated with reference to FIGS. 7 and 8. FIGS. 7 and 8 are cross-sectional diagrams of surface and through-conductive papers, respectively, which illustrate concepts of this invention. In FIG. 7, paper fibers 22 are shown flattened against paper support 19 so that none are in the path of current flow 20. In FIG. 8, paper fibers 50 are also flattened with little or no individual fibers 50 lying in the path of current flow 48, but rather a dense supporting base 49 is provided wherein all fibers are compressed and flattened, and thus less likely to be ignited. The craters 23 and 51 (10, 40 respectively) formed by spark discharge on the calendered bases of FIGS. 7 and 8 will be sharper and better defined, as illustrated, than the craters 24 and 52 formed on uncalendered substrates (see FIGS. 5 and 6).

Calendering is well known in the art of paper making and can be carried out to various degrees of surface

smoothness and gloss. Uncalendered papers as a rule have a rough surface due to gross variations in thickness from point-to-point and to a multitude of upstanding fibers ("fibrils").

It is possible to reduce the occurrence of surface fibers by sizing, and/or by machine-finishing techniques without a separate calendering operation. Papers designed "machine finish" or "high machine finish" are in this "intermediate-smoothness" category and have a smooth surface, relatively uniform thickness, and a nominal amount of surface fiber. Examples of such papers are: the "machine-glazed" and "machine-finished" papers produced by Consolidated Papers, Inc., by Kimberly-Clark Corp., and by Weyerhaeuser for electrostatic copying applications. These so called "electrostatic base papers" are very smooth, highly calendered or sized grades.

Calendering produces a smoother, denser, surface on paper depending upon the number of calendering roll nips used, the calender stack pressure, and other variables familiar to those skilled in the art. The ultimate smoothness is achieved by a process known as "super-calendering" which combines maximum stack pressure with the maximum number of passes through calender roll "nips".

Surprisingly, I have found that the degree of (unpleasant) odor reduction and the degree of enhancement in image clarity in an electroresistive paper is directly related to surface smoothness of the base sheet.

It will be understood that a supporting element having uniform thickness and smoothness will provide better recording clarity and more uniform print quality than a rough textured layer. And, it has not been heretofore realized that recording odor and odor persistence are traceable to loose or stray surface fibers from the (conductive or non-conductive) paper support.

Regarding the "burn-off fragrances" (masking agents) that are preferred, it is important to select materials that generate a pleasant odor in the presence of the recording spark. Many apparently-suitable fragrance formulations will burn, instead of evaporating, under these conditions. Burning produces an undesirable acrid odor with many materials, while evaporation retains the pleasing fragrance of the perfume agent. Thus, materials and conditions will preferably be chosen so as to foster evaporation, and not burning, of the additive.

It is not entirely understood how the recited fragrances function to mask and/or dissipate the objectionable "sparking" odors typical of electrosensitive recording processes. They may be absorbed into paper fibers and then evaporated upon the passage of a spark therethrough as mentioned.

I have discovered that certain so-called "flame fragrances" such as those candle fragrance oils which are used in the manufacture of scented wax candles, and incense fragrances used in burning or smoldering incense compositions, are also operable as perfuming agents (i.e., burn-off fragrances) for electrosensitive recording papers.

The art of perfumery traces its origins back to antiquity when fragrant woods and aromatic gums were burned for their pleasant, sweet, or in some cases irritating, odors. These odorous and malodorous substances have been used by mankind since the earliest times for religious, romantic, medicinal, and hygienic purposes. The word "perfume" itself derives from the Latin word "fumus" and can be taken literally as mean-

ing "through smoke" or "by means of smoke".

Although many perfume essences are sweet-smelling (fragrant), almost all of these scents lose their pleasant odor upon burning. Thus, it is the concept of this invention to prevent burning from taking place within the spark plasma, or in its aftermath, during electrosensitive recording; preferably effecting this by diluting the perfume essence in a volatile diluent fluid (carrier) which will evaporate upon the application of heat, and well before burning can occur. With this combination (essence plus volatile carrier), the true desired scent will emanate from the record blank during recording and any malodorous scent due to burning, charring, or smoldering will thereby be masked, modified or disguised.

Such a technique has not heretofore been applied to the field of electrosensitive recording. The function of the volatile diluent (carrier) is best analogized to candle making (see also: The "Modern Art of Candle Creating" by Don and Ray Olsen, A. S. Barnes and Company, Inc., Cranbury, N.J.); where ordinary commercial perfumes, colognes, incense, etc. (e.g. with an alcohol or water base are not compatible with wax) are completely consumed by the flame and dissipate with no aroma, oil-based scents not only have a pleasant aroma but also continue to release their fragrance while the candle burns.

The heavier mineral oils (known commercially as "white oils", being odorless and non-toxic) are inoperable in the present invention owing to their low volatility. These oils generally have a flash point about 300°F indicating the absence of low boiling fractions. But according to the invention, the fragrance essence carrier mixture (burn-off fragrance composition) must volatilize and not burn at some "off gas temperature range" well above ambient (room) temperature and below the related burn-off temperature. This will usually bracket this 300°F temperature, typically about 120°-400°F. Moreover, it is believed that, when, as preferred, the burn-off fragrance is impregnated into (at least one layer of) the spark medium (e.g. impregnating fibers therein), it will not only tend to thus provide a reservoir for prolonged perfume-release (e.g. fibers wicking it out) but will probably help to further discourage combustion (e.g. cooling and wetting such fibers, reducing the number of smoldering embers and/or cooling them). This is especially likely for typical spark recording which is so brief and applies relatively little total heat to the medium.

The class of operable "burn-off fragrances" includes floral, fruit, and forest perfume bases incorporated in a volatile diluent oil. The most commonly used diluents are odorless mineral spirits (e.g. alcohols), such as Humble Oil's "Isopar" and Shell Oil Company's "Shell-sol", ethyl alcohol, and certain glycols, such as propylene glycol. A preferred carrier is "Isopar-M", an odorless, "narrow cut" isoparaffinic hydrocarbon with a relatively moderately-high boiling point (volatility: 5% distillation at 410°F; 95% at 478°F; flash point 178°-200°F). These materials all have a flash point below 275°F, especially the odorless mineral spirits which are typically below 200°F.

A fairly wide range of preferred solvent carriers may be characterized:

1. they are capable of dissolving the perfume base or essence;
2. they are miscible with the coating composition (or, in rare cases, with the paper per se);

3. they do not have an objectionable, or persistent odor; and
4. they are sufficiently volatile (see above) to release the fragrance in the spark plasma, or from the smoldering record blank, before the fragrance is itself consumed by burning, charring or spark discharge.

Because the chemical additives of this invention typically include naturally-occurring products, or synthetic compositions comprising mixtures of complex molecular structures, it is not possible to completely identify all species that are operable or inoperable. Also, whether a particular scent is pleasant or offensive in a spark recording application is, of course, a subjective matter and lies outside the scope of this invention — the primary object of which is to preserve a particular scent for masking purposes, rather than to select and provide a special odor.

Nonetheless, for illustrative purposes, it should be noted that I have discovered that the following "burn-off fragrances" are quite suitable for most purposes: "Flame fragrance oils" of the floral variety, such as gardenia, honeysuckle, hyacinth, jasmine, lavender, lilac, lily of the valley, and rose — they being preferred for their non-offensive qualities, as are "forest fragrances" like appleblossom, bayberry, cedar, hollyberry and sandalwood.

"Fruit fragrances", such as banana, blueberry, cherry, grape, lemon, pineapple and the like are operable as masking agents, but are not readily acceptable in an industrial recording environment, such as in message or facsimile recording applications, or in confined quarters such as with aircraft or submarine recording systems.

It is not entirely understood how the recited fragrances function to mask "sparking" odor in the electrosensitive recording process. They may be absorbed or "wicked up" into paper fibers and then evaporated upon the passage of a spark therethrough.

On the other hand, they may be physically dispersed or atomized along with bits of base, intermediate, and top coat under the blasting action of the spark.

Although some amount of fragrant substance might be incorporated into the white top coating in accordance with the concept of this invention, I have found it necessary only to compound the perfuming agent in the base coat, or in the base and intermediate layers (e.g. base 18 in FIG. 5 or 49 in FIG. 6, and possibly intermediate layer 17, in FIG. 5, or 47, in FIG. 6) in order to achieve the desired effect of odor reduction.

One reason for not placing the fragrance in the top coat layer is that it will too readily be evaporated from this exposed surface, thereby giving off its fragrance prematurely, and also causing a strong, often undesirable, perfume odor to develop in packaged material (other than solely during the recording process).

In the following typical coating formulations, Examples 1 through 11 represent formulation details only, while Examples 12 through 32 illustrate finished electrosensitive recording media prepared from various ones of these coating formulations, together with the mixture results obtained thereby.

FORMULATIONS

Ground Coating Examples

The following Examples 1 through 5 are typical formulations used to prepare a "ground" coating, such as

coating 18 in FIGS. 5, 7.

EXAMPLE 1: Unscented Ground Coat

	Amount, grams	
"XYHL" Resin (a PVB-type resin by Union Carbide Co.)	15.0	5
Denatured alcohol	235.5	
Dioctyl phthalate	4.5	
"Vulcan XC-72R" Carbon Black by Cabot Co.	15.0	
	270.0	10

Dissolve the XYHL resin in its (two-part) solvent, a mixture of denatured alcohol and dioctyl phthalate plasticizer, until a clear solution is obtained. "XYHL" is a medium molecular-weight polyvinyl butyral resin produced by Union Carbide Co. Add the carbon black (a conduction-pigmenting additive) and grind in a one-pint paint can, by adding 300 grams of 4-mm diameter glass beads and shaking on a paint shaker for 45 minutes. "Vulcan XC-72R" is a high conductivity, fine particle, oil furnace black supplied by the Cabot Corporation.

Scented Ground Coats

EXAMPLE 2

Prepare a ground coating mixture in accordance with Example 1, then stir in 0.5 percent by weight of the candle fragrance "Maskit 2; M-778" supplied by the Stepan Chemical Company.

EXAMPLE 3

Prepare a ground coating mixture in accordance with Example 1, then stir in 0.5 percent by volume of the fragrance "Floral M-2877" supplied by the Stepan Chemical Company.

EXAMPLE 4

Prepare a ground coating mixture in accordance with Example 1, then stir in 0.5 percent by volume of the fragrance "Lemon M-2182" supplied by the Stepan Chemical Company.

EXAMPLE 5

Prepare a ground coating mixture in accordance with Example 1, then stir in 0.5 percent by volume of the fragrance "Citrogen K, M-1152" supplied by the Stepan Chemical Company.

Intermediate Coating Examples

The following Examples 6 through 10 are typical formulations used to prepare "intermediate coatings", such as coatings 17 and 47, described above (FIGS. 5, 7 and 6, 8 respectively).

EXAMPLE 6: Unscented Intermediate Coat

	Amount, grams	
"VYHH" Resin (a PVC-VV type resin by Union Carbide)	44.0	
Methyl Ethyl Ketone (MEK) — solvent	153.0	
Tri-cresyl phosphate (TCP) — plasticizer	9.0	
Toluene — solvent	110.0	
"NeoSpectra MK II" (by Columbian Carbon Co.)	5.0	
	321.0	

Dissolve the VYHH resin in its solvent, a mixture of MEK, TCP (plasticizer) and toluene until a clear solution is obtained. "VYHH" is a vinyl chloride-vinyl ace-

tate copolymer resin produced by Union Carbide. Add the "NeoSpectra MK II" carbon black and grind in a one-pint paint can by adding 300 grams of 4-mm diameter glass beads and shaking on a paint shaker for 45 minutes. "Neo-Spectra MK II" is an ultrafine particle, "channel black", supplied by the Columbian Carbon Company.

Scented Intermediate Coats

EXAMPLE 7

Prepare the intermediate coating mixture in accordance with Example 6, then stir in 0.5 percent by volume of the fragrance "Maskit 2, M-778", as in Example 2.

EXAMPLE 8

Prepare an intermediate coating mixture in accordance with Example 6, then stir in 0.5 percent by volume of the fragrance "Floral M-2877".

EXAMPLE 9

Prepare an intermediate coating mixture in accordance with Example 6, then stir in 0.5 percent by volume of the fragrance "Lemon M-2182".

EXAMPLE 10

Prepare an intermediate coating mixture in accordance with Example 6, then stir in 0.5 percent by volume of the fragrance "Citrogen K, M-1152".

The following is a typical example of a top coat formulation used to prepare top coats, such as coats 16 and 46. Other suitable top coat formulations are those cited in the U.S. Pat. No. 3,511,700 to Miro (See Examples 1 and 3).

EXAMPLE 11: Top Coat — Control, Unscented

	Amount, grams	
Alcohol soluble butyrate (ASB)	45.0	
Methanol	337.5	
Tri-cresyl phosphate (TCP)	15.0	
Aluminum stearate	20.0	
Zinc oxide (New Jersey Zinc No. HC-238)	100.0	
Zinc sulfide	35.0	
	552.5	

Dissolve the ASB resin in its solvent, a mixture of methanol and TCP. ASB is a product of the Eastman Kodak Company. Add the pigments (white) aluminum stearate, zinc oxide, and zinc sulfide and grind in a ½-gallon ball mill using 13/16-inch Burundum cylinders ("Burundum" is a trade name of U.S. Stoneware Co. for a grinding medium) for 15 to 20 hours. The "HC-238" zinc oxide is a high conductivity zinc oxide (white) pigment of the type disclosed in U.S. Pat. No. 3,887,632. The aluminum stearate, while not typical of conventional top coatings are not necessary, is an important additive found to enhance image clarity [as will any like compatible (white) metallic soap pigmenter, such as a zinc, calcium or iron stearate].

MEDIA EXAMPLES

The following Examples 12 through 32 are illustrative of finished media (electroresistive recording papers), prepared with formulations like the above, in accordance with the invention:

EXAMPLE 12

Improved "Compressed-Substrate",

"Front-Grounded" Medium

Select a highly-calendered substrate paper having good "solvent holdout" properties, such as Consolidated Papers, Inc., "Point Opaque", or Weyerhaeuser Company's Electrofax conductive base "J". Apply the unscented ground coat of Example 1 at a coating weight of 3 to 4 pounds per 3000 square feet by means of a wire-wound coating rod. After thorough drying, apply the unscented intermediate coat of Example 6 at a coating weight of 5.5 to 6.5 pounds per 3000 square feet. After this second layer has been thoroughly dried, apply the unscented top coat of Example 11 at a coating weight of about 9 to 11 pounds per 3000 square feet.

After thorough drying, place the record blank on a Xerox Telecopier 400 and record a standard facsimile test object. A pungent odor is emitted during the recording process. The odor is typical, resembling gunpowder, and is disagreeable, but somewhat subdued. However, the odor does not persist when the recording process is stopped (not perceptible after about one-half minute — this is much less than the usual "persistence time", on the order of several minutes or more). The sheet is removed from the machine and sniffed: no odor. The recording is clear and sharp.

The high "solvent-holdout" properties of this base will be recognized as inhibiting penetration of the relatively conductive resin into the paper base and to thus make the recorded image clear and sharper. According to this supplemental feature, this helps to assure that the conductive base coat is held up as a discrete layer above the fibrous paper support.

The highly-calendered (highly-compressed) nature of this paper base, according to this feature, will be recognized as keeping fibers confined within the substrate base to minimize any protrusion thereof, up into a super-coating and avoid the recited fiber-burning and resultant persisting odor problems.

Of course, an odor was discerned here nonetheless, it resembled gunpowder. This is believed due to combustion of the ASB or like cellulose. Those skilled in the art will recognize that the ground coating here (of Example 1) is intended to serve as a relatively high-carbon-loaded resin phase which thus exhibits high conductivity, while the intermediate coating (after Example 6) has relatively less percentage carbon and thus is of intermediate conductivity (as well as being dark in color) and the top coating (after Example 11) intended to be a "white" layer, masking the dark layer underneath, and, of course, has the lowest conductivity. This "conductivity gradation" (increasing top to bottom into the body of the record medium) is well-known in the art and is intended to optimize the sharpness and clarity of the spark-recorded image on such "surface recording" ("front-grounded") media. (Compare the embodiment in FIG. 7 described above.)

Perfumed Modifications; Ground Coat Only

EXAMPLE 13

Repeat Example 12, substituting the scented ground coat of Example 2 for that of Example 1. A much-reduced odor is emitted during the recording process; it is not as unpleasant, nor does it persist. Here, of course,

the compressed substrate of Example 12 is combined with a scented undercoat. The faint, pleasant "lemony" odor released during recording (no gunpowder smell) ceased abruptly (within a few seconds) upon cessation of recording. Workers in the art will agree that it is quite surprising, and pleasing, that the usual disagreeable recording smell could be so easily dispelled. Of course, without the "compressed substrate" somewhat more, and possibly more persistent, odor might be experienced.

EXAMPLE 14

Repeat Example 12 substituting the ground coat of Example 3 for that of Example 1. Results are similar to Example 13 except the "burn-off fragrance" is different.

EXAMPLE 15

Repeat Example 12 substituting the ground coat of Example 4 for that of Example 1. Results are similar to those in Example 13 with different fragrance.

EXAMPLE 16

Repeat Example 12 substituting the ground coat of Example 5 for that of Example 1. Results are similar to those in Example 13, with different fragrance.

EXAMPLES 17-20: Multi-Layer Perfuming
(Ground/Intermediate)

Repeat Examples 13 through 16 using, in turn, the following ground/intermediate coat combinations with like fragrances: Examples 2/7, 3/8, 4/9 and 5/10.

In each case, the results are somewhat superior to those in Examples 13 through 16. It is theorized that this may be so because both ground and intermediate layers include odor masking agents (rather than merely in a single coating). Thus, greater fragrance volume is volatilized and from more disparate sources.

EXAMPLES 21-25: Calendering Eliminated

Repeat Examples 12 through 20 using an uncalendered sheet having a high degree of loose surface fibers, such as a duplicator bond or a saturating paper. Results are similar to those obtained before, except that the odor is more persistent, continuing to emanate from the record blank for some time after recording ceases (especially for Example 21). The recorded image is somewhat less clear, with resolution being relatively poor. It will be appreciated that with such a rough fibrous base, the loose fibers projecting up into the super-coating(s) are probably responsible for the persistent burning smell.

As indicated above (Example 12), it is preferable to compress the fibers down into the body of the base, and/or to coat them and so isolate them, where it is important to minimize this fiber-projection problem for such surface-conductivity spark recording. It will be appreciated that the relationship between the persistent burning odor and the smoothness and fiber-free character of the base (contact surface thereof) is a significant parameter to bear in mind for preparing improved spark-recording media. Also, the record is less clear and resolution is poorer without such "compressing".

EXAMPLE 26: "Machine-Finished" Substrate

Using a carbon-filled conductive base paper such as Riegel Paper Corporation's "MF, Black Facsimile"

base, or Knowlton Paper Company's "Grade 506L", then apply the intermediate coating (unscented) of Example 6 at a coat weight of 5.5 to 6.5 pounds per 3000 square feet by means of a wire-wound coating rod. After thorough drying, apply the (unscented) top coat of Example 11 at a coating weight of about 10 pounds per 3000 square feet.

Test the dried record blank in the same manner as Example 12, recording with "through-spark" equipment like the "Deskfax" spark recorder of Western Union. A pungent odor is emitted during the recording process which is more intense than that observed in the case of Example 12, but less than for Example 21. Also, the odor persists for several minutes after the spark-recording process is stopped. This is apparently so because no odor-masking agent ("burn-off fragrance") is provided, nor is the base paper fully calendered to thereby protect against fiber penetration into the spark plasma zone.

A moderately clear recorded image is obtained. Of course, the conductive-base paper could additionally be calendered, or otherwise compressed, to further ameliorate its odor emitting characteristics.

EXAMPLES 27-30: Scent Intermediate Coat

Repeat Example 26, substituting, in turn, the intermediate coating formulations of Examples 7, 8, 9 and 10 for that of Example 6. An odor which is non-pungent and relatively pleasant is emitted in each case, varying in character as with Examples 17 through 20, but less pronounced. Record clarity and sharpness is unchanged.

EXAMPLE 31: Non-Fibrous Substrate

Repeat Example 12 (compressed substrate; no scenting), but substitute a polyester film material for the paper base. Mylar film (by DuPont) is quite satisfactory, preferably in conjunction with a suitable lacquer adhesion coating applied thereon, as known in the art. The results will be a clearer and sharper recording, with a similar "gunpowder" odor; however, the odor will be quite short-lived.

It will be apparent that the use of such polyester film gives a stronger substrate, as well as one which resists penetration of conductive fluids, such as the carbon-loaded resin, and which also provides a very smooth base for precise application of the super-coatings. Of course, "projecting fibers" and the attendant "burning" are entirely eliminated.

EXAMPLE 32: Metallic Substrate

Repeat Example 26 (machine-finish; no scenting), but substitute a conductive metal sheet for the base paper. Preferably a "smooth, velvet-finish" aluminum foil, about 10 mils thick, is used with the intermediate and top coatings applied thereon as in Example 26.

It will be observed that the record image is considerably clear and sharper, with better resolution, and that the "burning" smell emitted is very faint or non-existent and does not persist at all.

CONCLUSION

In the foregoing Examples, the amount of specified fragrance oil used can be varied up to a few weight percent (preferably from about 0.05 to about 1.0 weight-percent), depending upon the degree of odor release and masking desired. The upper limit is largely determined by the specific fragrance used and by the

amount of scent that can be used judiciously without having the fresh record media exhibit too much scent.

In each layer, other resins and resin combinations can be substituted for the ones specified, provided the three coatings — ground, intermediate, and top — are mutually insoluble. Thus, the application of one coating should not cause the under-layer to swell or dissolve appreciably.

The type and amount of carbon black, zinc oxide, or zinc sulfide pigment can be varied over a rather broad range provided the surface resistivity of the base coating lies between about 100 and 1000 ohms per square cm; while that of the intermediate layer lies between about 900 and 5000 ohms per square cm; and that of the top coating lies between about 1×10^5 and 1×10^7 ohms per square cm. Of course, a higher concentration of such pigments produces increased color; unfortunately, it also increases conductivity, and one characteristic must be traded-off against the other.

Workers in the art will perceive that the "burn-off fragrance" compositions and related features and techniques (e.g. fiber compression) according to the invention may take various forms other than those described above, modified alone, or cumulatively, yet within the spirit and scope of the subject teaching and claims. Workers will also perceive that substantial useful advantages are derived by using the invention, either as indicated above or in other analogous ways. It should be understood that in addition to the unexpected and useful advantages and properties described above, these compositions have a number of other such advantages and properties. For instance, other scent materials may be used insofar as they are compatible with the medium, such as certain candle fragrance oils sold by Lautier Fils, Inc. (Parsippany, New Jersey) or certain incense and flame fragrant oils prepared by Grommes Aromatics Company (Los Angeles). Also, such scents may be differently applied or incorporated into the record blank, e.g. as a treatment of the fibers applied during the paper-making process, or as a spray or mist applied to the record blank before or during spark discharge. Alternatively, and less preferably, a scented ("burn-off fragrance") layer may be applied at one, or several, locations beneath the top coat (e.g. as a coating compressing the fibers on the substrate), or integral with the substrate itself where such is likely to be volatilized during recording.

In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

As various changes could be made in the above constructions and methods without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. An improved spark-discharge recording medium comprising:
 - a base support;
 - a dark colored conductive layer on said support; and
 - a contrasting light colored surface layer combustible at the temperature developed during passage of marking current through said medium to selectively reveal the underlying dark layer with attendant generation of smoke, objectionable odor and combustion debris, wherein said medium includes an effective amount of a fragrance oil having a

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flash point above said temperature and a vaporization point at said temperature so as to vaporize without burning during said discharge to develop a pleasant aroma.

2. A medium according to claim 1 in which each layer comprises a pigment dispersed in a film-forming resin and said fragrance oil dissolved in a compatible solvent is compounded into at least one of said layers.

3. A media according to claim 2 in which the solvent is a volatile mineral oil having a flash point from 120°F to 400°F.

4. A media according to claim 2 further including an intermediate dark layer between said conductive layer and said surface layer comprising a conductive pigment dispersed in a film forming binder having a resistivity intermediate the conductive and surface layers and in which the surface resistivity of the conductive layer is from 100 to 1,000 ohms/cm², the surface resistivity of the intermediate layer is from 900 to 5,000 ohms/cm² and the surface resistivity of the surface layer is from 10⁵ to 10⁷ ohms/cm² and said intermediate layer also includes fragrance oil.

5. A media according to claim 2 in which the base support has a smooth surface.

6. A media according to claim 5 in which the base support is a paper sheet having a machine-finish supercalendered surface.

7. A media according to claim 2 in which the fragrance oil is present in the conductive layer.

8. A media according to claim 7 in which the conductive layer comprises a conductive carbon black pigment dispersed in an organic resin binder.

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9. A media according to claim 8 in which the surface coat comprises a white inorganic pigment dispersed in a combustible organic film-forming binder.

10. A media according to claim 7 in which the fragrance oil is a volatile, non-burning, non-tar producing candle fragrance oil.

11. A media according to claim 10 in which the fragrance oil is selected from floral, fruit and forest perfume oils.

12. A media according to claim 11 containing from 0.05 to 1.0 weight percent of the fragrance oil.

13. A media according to claim 12 in which the fragrance oil is present in said layer in a relative amount of 0.5 parts by volume.

14. A method of reducing the persistence and quality of odor emanating from spark discharge recording medium comprising the steps of:

calendering the top surface of a paper support to a glossy, machine finish to reduce projection of combustible fibers into the superimposed layer;

coating a first dark conductive layer comprising conductive pigment dispersed in a film-forming binder thereon;

coating a second lightly-colored surface layer comprising white inorganic pigment dispersed in film-forming binder on the first layer; and

incorporating into at least one of said layers 0.01 to one percent by weight of a fragrance oil having a flash point below the temperature developed during spark discharge recording and volatile at said temperature.

15. A method according to claim 14 in which the oil is dissolved in a solvent compatible with the binder resin of the layer and having a flash point below said temperature.

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