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THERMOGRAPHIC STENCIL SHEET AND METHOD OF MAKING AN IMAGED STENCIL SHEET

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ABSTRACT OF THE DISCLOSURE

A finely divided silica gel is dispersed in a heat-flowable thermographic stencil sheet coating composition of cellulose acetate butyrate film-forming material and plasticizing material partially but incompletely compatible with the film-forming material, to improve the oil transfer and blocking characteristics of the stencil sheet. The stencil sheet may be imaged by exposing an original in contact with the sheet to infrared radiation to generate heat in the image areas of the original sufficient to render the composition flowable in the image areas of the stencil sheet, and causing the composition to flow from the image areas to thereby form corresponding ink-transmitting openings in the stencil sheet.

BACKGROUND OF THE INVENTION

This invention relates to a thermographic stencil sheet of the type which includes a layer of a heat-flowable composition and to a method of making an imaged stencil sheet therewith by subjecting image areas of the stencil sheet to heat generated by infrared ray absorption.

Copending U.S. patent application Ser. No. 674,153, filed Oct. 10, 1967, now abandoned, by the present inventors Anderson and Schick discloses a thermographic stencil sheet including an ink-pervious base sheet and an ink-impervious coating thereon of a heat-flowable composition of cellulose acetate butyrate film-forming material and plasticizing material partially but incompletely compatible with the film-forming material. The stencil sheet is now in widespread commercial use. It is employed preferably in a stencil sheet assembly including a contacting absorbent sheet on one surface thereof, and a more rigid backing sheet on the opposite surface thereof and to which the absorbent sheet and the stencil sheet are mounted. In use, an original, such as a typed or printed sheet, is inserted between the stencil sheet and the backing sheet, and the assembly is exposed to infrared radiation on the face side of the absorbent sheet in a thermal copier such as a Thermo-Fax machine (3M Company). Heat is generated in the radiation absorptive graphic portions of the original to cause the stencil sheet composition to flow in corresponding areas and thereby produce corresponding image openings in the stencil sheet. The composition rendered flowable is absorbed by the absorbent sheet and/or adjoining areas of the stencil sheet. The original and the absorbent sheet are separated from the imaged stencil sheet, the stencil sheet and the backing sheet are placed on a mimeograph duplicating machine followed by separation of the backing sheet, and the machine is operated to produce multiple mimeograph copies of the original.

It was found in use that "oil" was transferred from the stencil sheet to the original in the image areas. The oil frequently broadened and feathered the copy on the original (smudging) and the presence of oil on the original was not a desirable condition. The smudging of the original affected the imaging speed in subsequent exposures, owing to the broadening of the image characters or transfer from the original to the stencil sheet. Subsequent performance was affected when the original was removed from the file for rerun, or in the event that optimum exposure was not used in imaging the first stencil.

It would be desirable to reduce the oil transfer to more desirable limits while preserving the advantageous properties of the stencil sheet of our aforesaid copending application.

In copending U.S. patent application Ser. No. 27,135, filed Apr. 9, 1970, by the present inventors Anderson and Schick, an improved thermographic stencil sheet is disclosed, which exhibits low oil transfer. The stencil sheet includes a heat-flowable composition characterized by forming a cooled melt having a defined pourable liquid volume, and a plasticizing material in the composition characterized by defined tack and aniline point limits.

More particularly, the improved thermographic stencil sheet of the foregoing application comprises an ink-pervious base sheet, and an ink-impervious coating thereon of a heat-flowable composition of film-forming material comprising cellulose acetate butyrate, and plasticizing material having (a) a tack index, as defined hereinafter, of at least about 10, and (b) a maximum mixed aniline point of about 110° F., the said composition initially forming a clear homogeneous single phase melt at a maximum temperature of about 320° F. and forming a solid-liquid two-phase mixture when cooled from the melt to room temperature, at least one phase of the said mixture incorporating substantial proportions of both the film-forming material and the plasticizing material, the mixture having a pourable liquid volume which is a maximum of about one-fourth the volume of the solid phase, the said composition being soluble in a volatile solvent and forming a substantially clear homogeneous continuous imperforate coating when deposited from a solution thereof, and the said coating being provided on the base sheet by deposition of the composition on the base sheet from a solvent solution thereof, the melting point of the coating being in the range of about 150–320° F.

The improved stencil sheet of the copending application has markedly improved oil transfer properties and in many cases also provides improved copy quality. Nevertheless, there remains room for improvement. Thus, various embodiments of the copending application do not exhibit optimum results for all of the more significant stencil performance characteristics, including durability, imaging speed, imaging quality, oil smudging and oil transfer, and blocking. Frequently, blocking is less than optimum when oiling is reduced to a minimum. In some cases, optimum oiling properties can not be achieved, although oiling is improved. At times, imaging speed or imaging quality is less than optimum.

It would be desirable, further, to achieve the improved oil transfer properties of the copending application while improving the stencil sheet thereof in one or more respects, so as to approach optimum performance characteristics for a thermographic stencil sheet.

SUMMARY OF THE INVENTION

The present invention provides an improvement in a thermographic stencil sheet of the type disclosed in the application Ser. No. 674,153, which reduces oil transfer while maintaining performance characteristics. While not so limited, the invention is especially advantageous when employed in combination with the aforesaid improvement of the subsequent copending application, the combination providing a thermographic stencil sheet approaching optimum all-around performance in numerous embodiments.

In the invention, a finely divided silica gel is dispersed in the heat-flowable coating composition of a thermo-

graphic stencil sheet, the composition including film-forming material comprising cellulose acetate butyrate and plasticizing material partially but incompletely compatible with the film-forming material.

The silica gel is dispersed in the coating composition in a proportion of about 1–20% by weight of the film-forming and plasticizing materials. Preferably, the silica gel has an oil absorption capacity of at least about 90 lbs./100 lbs. It is further preferred that the silica gel have a maximum average particle size of about 10 microns.

In a specific preferred embodiment of the invention, a combination of conditions and materials is provided, embodying the conditions and materials previously disclosed to provide improvements in the basic stencil sheet, as described above, and the provision of silica gel in the coating composition, as disclosed herein.

The invention also provides a method of making an imaged stencil sheet, wherein the thermographic stencil sheet is employed in contact with a graphic original, image areas of the stencil sheet are subjected to heat generated in the original by infrared ray absorption to render the composition flowable in the stencil sheet image areas, and the composition is caused to flow from the vimage areas and thereby form corresponding ink-transmitting image openings in the stencil sheet.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The thermographic stencil sheet includes a stencil base tissue sheet that may be formed of any suitable fiber, such as abaca, abaca and wood fibers, kozo fiber, or polyester fibers, loosely arranged to provide a foraminous, highly permeable tissue. The tissue may weigh about four and one-half to twelve pounds per 3,000 sq. ft. (24" x 36", 500 sheets). A heat-flowable coating composition, which is solid at ambient temperature, is applied to the base sheet at a rate of about 14 to 24 lbs. (dry basis), preferably about 20 lbs. per 3,000 sq. ft. The coating composition melts in the range of about 150°–320° F., more preferably 200–300° F.

The heat-flowable coating composition includes cellulose acetate butyrate film-forming material, which is capable of forming a continuous, cohesive, flexible, ink-impervious film. The film-forming material is plasticizable to melt in the range of about 150–320° F. The film-forming material is employed in a proportion in the range of about 8–50%, preferably about 8–30%, and more preferably about 14–23% by weight of the coating composition, including the film-forming and plasticizing materials and exclusive of additives thereto. The volume ratio of the film-forming material to the total plasticizing material in the coating composition preferably is in the range of about 1:13 to 1:3.5.

Of the available grades of cellulose acetate butyrate, it is preferred to employ those having values of about 35–55% butyryl content, more preferably above about 49%, and about 1.5–13% acetyl content, by weight. The hydroxyl content varies up to about 4.5% by weight, and it is preferred that the hydroxyl content be below about 0.4%. The viscosity is about 0.15–6 seconds, by A.S.T.M. Method D–1343–54T in Formula A, A.S.T.M. Method D–871–54T. The melting or softening points range from about 265 to 360° F.

The film-forming material is combined in the coating composition with a plasticizing material partially but incompletely compatible therewith. Such plasticizing material is defined to mean material which when heated with the film-forming material in the proportions used forms a clear homogeneous single phase melt, and which when cooled from the melt to ambient or room temperature forms a two-phase mixture, at least one phase of the mixture incorporating substantial proportions of both the film-forming material and the plasticizing material. The materials employed in the composition initially form a single phase melt at a maximum temperature of about 280–320° F., varying with the specific composition. Such temperature is referred to as the compatibility temperature of the composition. It is preferred that the compatibility temperature be at least about 120° F., and in further preferred embodiments of the invention, the compatibility temperature is above about 170° F.

Upon cooling below the compatibility temperature, the liquid separates into two phases. The mixture remains fluid over a temperature range, and then the phase containing the major proportion of the film-former gradually hardens to a solid as the coating cools to room temperature. The liquid phase may be trapped by the gel structure of the solid phase at room temperature, or it may separate into a discrete liquid component.

A characteristic of the improvement of the Anderson and Schick copending application is that the foregoing mixture at room temperature has a maximum pourable liquid volume of about one-fourth the volume of the solid phase, and it is preferred that the pourable liquid volume be a maximum of about one-eighth the volume of the solid phase. For example, the mixture is cooled to room temperature with stirring, and its consistency is observed. A uniform gel or slush, having no solid separation, generally is optimum for low oil transfer. The mixture may separate into solid and liquid fractions, the solid being particulate or in the form of a ball, from which a liquid may be poured. It is the volume of such pourable liquid with reference to the solid content of the mixture which is referred to in connection with the above pourable liquid volume maximums.

The foregoing characteristic of the improvement of the copending application constitutes a preferred condition in the present invention. However, the invention is not limited thereto, since improved results are also obtained at higher pourable liquid volumes, as illustrated in the examples.

The plasticizing material having partial but incomplete compatibility with the film-forming material may constitute a single plasticizer, or may include a plurality of plasticizers. The plasticizers are substantially non-volatile substances which serve to modify the physical properties of the film-forming material, including the melting or softening point, compatibility, and/or flow properties. They may be either liquid or solid at temperatures from ambient temperature up to close to imaging temperature, but at least must be liquid when mixed with other plasticizers at imaging temperature.

The plasticizers generally fall into three groups as regards compatibility with the film-forming material: partially but incompletely compatible, incompatible, and compatible substances. Certain of the partially compatible plasticizers may be employed as sole plasticizers. Alternatively, two or more plasticizers having individual compatibilities varying from complete compatibility to complete incompatibility may be employed, so long as the plasticizers together provide the proper balance of compatibility with the film-forming material. When a plurality of plasticizers is employed, it is preferred that they be compatible with each other at room temperature, forming a single phase mixture after heating together and cooling.

The above-described composition having the defined maximum pourable liquid volume constitutes a relatively compatible composition. When such a composition is employed in the stencil coating, the coating may suffer from blocking, owing to tackiness accompanying increased compatibility. Blocking is a condition of adherence or sticking to adjacent stencil material in a roll, or sticking to the original or the top tissue during imaging, which causes pinholing. As disclosed in the latter application of Anderson and Schick, plasticizing material can be formulated on the basis of defined tack limits to minimize blocking. In particular, a plasticizing material, including

one or more plasticizers, is employed which has a tack index of at least about 10, determined as follows:

The "Tack Rolling Ball Method" of the Pressure Sensitive Tape Council (Glenview, Ill.) was modified for a lower tack level, and the modified method is identified herein as the "modified rolling ball method." The apparatus included a glass plate, 8½" x 11" supported in horizontal position. A second glass plate, 3" x 6", was mounted with its 3" edge abutting the 8½" edge of the first plate, with their upper edges or corners in aligned contact with each other. A ball holder was affixed to the smaller plate to release a ball ½" from its outer end. The outer end of the smaller plate was elevated so that the surface of the plate at the point of ball release was 0.203" above the horizontal plane of the upper surface of the large plate. The apparatus thus was arranged for releasing a steel ball on the small plate to roll down 5½" of the small plate and on to the large plate. Steel balls were used having a diameter of 7/16" and weighing 5.48 grams.

In the test, a film of the plasticizing material to be tested is cast on the large plate and drawn down to a thickness of ½ mil. The film is cast at a temperature such as to render the plasticizing material sufficiently fluid, and is cooled, if necessary, for measurement at room temperature (77° F.). The cast film is drawn down with a rod or other suitable means to provide the film thickness of ½ mil.

A ball rolling across the film will experience a decelerating force proportional to the velocity of the ball and the tackiness of the film. Liquid viscosity also has an effect, minimized by employing the very thin film. In addition, an experimentally determined viscosity factor is applied to the results.

Tack measurements are made in inches of ball roll on the larger plate bearing the film, measured to the point the ball stops. The tackier the material, the shorter the distance of ball roll. The tack index referred to herein and in the claims is determined by measurement of the amount of ball roll on the horizontal plate, in inches, multiplied by the $\log_{10}$ of the viscosity of the plasticizing material in centipoises at 77° F.

A tack index of at least about 10 constitutes a preferred condition in the present invention. However, the invention is not limited to this condition, since improved results are also obtained at lower tack indices, as illustrated in the examples.

As disclosed in the latter application of Anderson and Schick, the above-described conditions of maximum pourable liquid volume from a cooled melt of the composition of film-forming and plasticizing materials, and of a minimum tack index will in general serve to identify coating compositions, both in their materials and in their relative proportions, which will provide low oil transfer with minimized blocking. There are, however, exceptions, and it was found that the exceptions noted are excluded by limitations on the aniline point of the plasticizing material, the aniline point serving as an indication of the compatibility of the plasticizing material with the film-forming material. Thus, the plasticizing materials employed are relatively compatible with the film-forming material, while remaining partially but incompletely compatible therewith. In general, a maximum mixed aniline point of about 110° F. is specified for the plasticizing material.

A maximum mixed aniline point of about 110° F. for the plasticizing material constitutes a preferred condition in the present invention. However, the invention is not limited to this condition, since improved results are also obtained at higher aniline points, as illustrated in the examples.

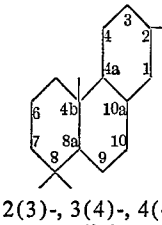
Mixed aniline point as referred to herein and in the claims is determined by A.S.T.M. Test D–1012–62. It is the minimum equilibrium temperature of a mixture of 2 volumes of aniline, 1 volume of sample, and 1 volume of n-heptane of specified purity. Straight aniline point is determined according to the A.S.T.M. test, and is the minimum equilibrium temperature of a mixture of 1 volume of aniline and 1 volume of sample. For formulating purposes, it is generally useful to mix high aniline point material with a low aniline point, low tack material such as Hercolube A (described hereinafter), in a 50:50 volume ratio, and run the aniline point of the mixture. Similarly, it is useful to mix low aniline point material with high aniline point material such as Mobilsol L (described hereinafter). Theoretical aniline points may be determined in this manner for materials which otherwise cannot be measured or can be measured only with difficulty. Theoretical aniline points referred to hereinafter were determined in the foregoing manner.

The plasticizing material and proportions thereof are selected on the basis of the herein-defined physical properties. Numerous and diverse materials may be employed, in a variety of combinations and relative proportions. Most frequently, a plurality of individual plasticizers are combined to achieve the specified physical conditions and optimum results. When the plasticizing material satisfies the basic conditions, the proportions of individual plasticizers thereof then may be adjusted within the defined limits to achieve optimum properties.

The plasticizing material is oleaginous or oily in nature, that is, it contains one or more oleaginous plasticizers. While numerous oleaginous plasticizers may be employed, it is presently preferred to employ one or more members selected from the group consisting of mineral oil, castor oil, hexadecyl alcohol, polypropylene glycol monobutyl ether, polyoxyethylene ethers of lanolin alcohols, pentaerythritol tetra-esters of aliphatic acids having from 5 to 10 carbon atoms, and trimethylol propane tri-esters of aliphatic acids having from 5 to 10 carbon atoms. An oleaginous plasticizer or mixture of plasticizers may be present in a proportion in the range of about 5–85% by weight of the film-forming material and plasticizing material, such materials being referred to herein as the active materials, excluding the silica gel and other materials which are neither film-formers nor plasticizers, such as inert solids and other materials performing other functions.

It is further preferred to employ plasticizing material containing mineral oil, an ester of an aliphatic acid having from 5 to 10 carbon atoms, as described above, or a mixture of the two. The mineral oil preferably is employed in a proportion of about 5–70% by weight of the composition of film-forming material and plasticizing material, more preferably, 10 to 50%. The aliphatic acid ester is employed in a proportion of about 5–85% by weight of the composition, preferably 15–55%.

A valuable class of plasticizers generally employed with one or more other plasticizers in the invention constitutes materials having the nucleus:



wherein the 1(2)-, 2(3)-, 3(4)-, 4(4a)-, 4a(10a)-, 9(10)- and 10(10a)-carbon atom linkages are selected from the group consisting of single bonds and double bonds, and the nucleus contains from 0 to 3 non-adjacent double bonds, all of which are located in such positions. Such materials provide low oil transfer and/or low tackiness properties. They may be employed in proportions of about 5–75%, preferably 15–55% by weight of the film-forming and plasticizing materials.

The materials having the foregoing nucleus include lanolin steroils, which serve to impart low tackiness.

The materials including such nucleus also include the acid constituents of rosin, known as resin acids, and their

derivatives, including derivatives of the resin acids both in refined form and as present in rosin, about 90% of which constitutes resin acids. The resin acids are chiefly the abietic acid type, and abietic acid is the major constituent of the acids. The resin acid derivatives are preferred as having greater stability than the resin acids.

Preferred derivatives of the resin acids include hydrogenated resin acids, esters of resin acids, dimerized resin acids, zinc and calcium di-resin acid carboxylates, hydroabietyl alcohol, and esters of hydroabietyl alcohol. Preferred esters include the methyl, pentaerythritol, glycerol, phthalate, and polyol esters, the latter including particularly the diethylene and triethylene glycol esters. Such materials are in general relatively compatible with the film-forming material and with other plasticizers, and they serve to impart low oil transfer and/or better durability to the coating composition, partially as a result of the higher viscosity they impart.

A formulation for high viscosity may assist valuably in the provision of a low oil transfer composition. With higher viscosity, compatibility of the plasticizing material with the film-forming material may be and often preferably is reduced with the aniline point of the plasticizing material being higher. Also, the tackiness of the plasticizing material may be higher, and the pourable liquid volume from the cooled composition melt may be greater. However, the copy quality may suffer in some cases.

The film-forming and plasticizing materials of the coating composition are soluble in a volatile solvent and are selected and blended in proportions so as to form a substantially clear homogeneous continuous imperforate coating when deposited from a solution thereof, the coating then being provided on the base sheet by deposition of the composition thereon from such solution. In this connection, reference to clarity of the coating, as an index of compatibility, is to be understood as being exclusive of the effect of additives other than the active or basic film-forming and plasticizing materials, i.e., the silica gel, and other additives such as solids incorporated for other purposes, fillers and others. Reference to clarity is also exclusive of the opacifying effects of materials having an inherent opacity, such as waxy materials, and of the presence of materials which are solid at room temperature and are incorporated above their solubility limits at room temperature.

The composition of film-forming and plasticizing materials preferably is completely soluble in a volatile solvent at a temperature below about 140° F., more preferably, at room temperature. The preferred compositions are soluble in organic solvent mixtures of aromatic hydrocarbons, and aliphatic esters and/or aliphatic alcohols, and are deposited on the base sheet from a solution therein by evaporation of the solvent. The composition deposited in this manner forms a uniform gel on the base sheet, which is irreversibly physically altered when heated to its melting point.

The film-forming and plasticizing materials are selected and blended in proportions so as to form a stencil sheet coating melting in the range of about 150–320° F. The stencil coating may melt at a temperature from below to above the compatibility temperature, as described above. Reference to the melting point of the coating herein means the temperature at which a free film of coating on a vertical surface becomes liquid enough to flow. (A free film is obtained by depositing the coating from solvent onto a non-porous surface.)

A finely divided silica gel is dispersed in the composition of film-forming and plasticizing materials, having the foregoing characteristics, in a proportion of about 1–20% by weight of the film-forming and plasticizing materials. The silica gel is a low infrared absorbing solid that alone may serve to reduce oil migration and minimize or obviate the problems occasioned thereby, such as smudging of the original image and/or the presence of oil on the original following imaging. Most advantageously, the silica gel is incorporated in a composition formulated in accordance with the disclosure of the latter application of Anderson and Schick, and therefore already having improved oil transfer characteristics. The complete composition of film-forming material, plasticizing material, and silica gel then may be formulated to maximize the characteristics of imaging speed, imaging quality, and durability while minimizing oil transfer and blocking. In this connection, it will be understood that individual characteristics may vary somewhat from composition to composition, and some compositions will be superior to others, while generally porviding markedly superior stencils over all. It is thus possible to select compositions with regard to cost, availability, manufacturing and various other considerations, which may at times weigh more heavily than the need for the highest rating in one or more of the stencil sheet characteristics.

The preferred silica gel has an oil absorption capacity of at least about 90 lbs. per 100 lbs. for broadest, most versatile application. Silica gel having an oil absorption capacity above about 300 lbs. per 100 lbs. is further preferred. Oil absorption capacity as referred to herein is determined according to A.S.T.M. Method D–281–31, based upon the absorption of linseed oil.

The silica gel is quite effective in reducing oil transfer propertes, even in small amounts. It also contributes greatly to blocking resistance, tending to eliminate sticking of the stencil material to itself in a roll and/or sticking to the original or the top tissue sheet during imaging, which causes pinholing.

An important aspect of the invention concerns the imaging performance of the composition in the presence of the silica gel. Thus, it is essential that the plasticizing material in the composition continue to perform its functions in providing a flowable composition which is immediately removed or released from the image areas upon imaging. It was discovered that while the silica gel acts to prevent undesirable transfer of the plasticizing material, it nevertheless does not present a problem in forming a stencil image in the proportions employed.

It will be found at times that the higher proportions of silica gel tend to reduce the imaging speed and the image quality. These effects may be counteracted by adjustment of the plasticizing materials. Ultimately, imaging speed and imaging quality fall off too greatly, and the transfer of oil commences to increase owing to the longer imaging time. The above-described upper limit of 20% of silica gel represents approximately the upper limit for an acceptable stencil employing one of the grades of silica gel which have been evaluated.

As illustrated in the examples, the preferred ranges of proportions for the several grades of silica gel may not be coextensive, but may overlap. Thus, the high oil absorption grades are more effective in lower proportions, and the low oil absorption grades maintain overall performance better at the higher proportions. In general, the optimum proportions for all of the grades of silica gel evalutaed are found in the range of about 2–12% by weight of the film-forming and plasticizing materials, especially for the high oil absorbing grades, preferably having an oil absorption capacity above about 300 lbs./100 lbs. The results obtained at various proportions are subject to variation among otherwise differing compositions.

It is preferred that the maximum average particle size of the silica gel be about 10 microns. With larger particles, there is an increasing tendency towards settling in coating operations. It further appears preferable that the silica gel particles fall within the range of about 0.5–12 microns, to the extent of 90% of their weight, i.e., there being a maximum of about 5% of the particles below and about 5% of the particles above such range. It appears that particles of smaller size are less effective. In this connection, the particle size referred to is an agglomerate

size as conventionally identified, whereas the ultimate particles in the agglomerates are much smaller, e.g., 0.01–0.02 micron.

Silica gel thus may be included in the coating composition to marked advantage. Oil transfer is materially reduced, blocking tendencies are counteracted, and overall high quality stencil sheets may be produced. Silica gel may be employed without affecting imaging quality and imaging speed. It may be employed in relatively small quantities and without adverse effect on the stencil sheet. Silica gel disperses uniformly throughout the coating composition.

For optimum results, it may be necessary to adjust the ingredients of the coating composition and their proportions on the basis of observed results. That is, adjustment may be made to improve uniformity, featherness, and brokenness of the imaged characters, oiliness, blocking, speed of imaging, and durability. The majority of the stencil sheets illustrated herein may also be imaged mechanically, as by typing, which constitutes a substantial advantage. Adjustment of the materials and proportions also may be made to provide optimum typing sensitivity.

The stencil sheet may be imaged in a conventional thermographic machine, such as a roller-type copier as represented by Copy-Rite Model CF 8 (Polyfax Corporation), and a belt-type copier such as a Thermo-Fax Model 45CG "Secretary" machine. A tungsten filament lamp or other suitable source of infrared radiation is employed for imaging. A printed original in contact with the stencil sheet is exposed to radiation substantially instantaneously, i.e., on the order of about 0.03 to 0.1 second, to generate a temperature rise in the image portions of the original from about ambient temperature to a temperature sufficient to produce a temperature in the image portions of the stencil sheet in the range of about 150–320° F.

The coating composition in the stencil sheet is reduced to a flowable condition substantially instantaneously and is absorbed by the absorbent sheet or into adjacent areas of the stencil sheet immediately thereafter, to leave ink-transmitting image openings in the stencil sheet. The openings are bridged by the fibers of the stencil base sheet, which is ink-pervious, and the base sheet fibers serve to retain letter centers and the like in place. The imaged stencil sheet is separated from the original and the absorbent sheet for use as a duplicating master.

In the examples which follow, the coating compositions were formulated in a solvent mixture of 92.8 parts of toluene, 26.4 parts of ethyl alcohol (95% denatured, U.S. government Formula C), and 66.4 parts of 99% ethyl acetate, in parts by weight. The plasticizing materials were dissolved in a portion of the solvent mixture at room temperature, and a solution of the cellulose acetate butyrate in another portion was added thereto. A dispersion of silica gel in a third portion of the solvent mixture was added to the solution and mixed well. In this manner, the materials of each coating composition were incorporated in the solvent mixture at a concentration of about 30–35% by weight.

Stencil base tissue sheet material made of abaca fiber was coated and impregnated with the coating composition. The tissue weighed 6.7 lbs. per 3,000 sq. ft. The sheet material was coated with the composition by contacting its bottom surface with the surface of a quantity of coating composition in a dish, removing excess fluid by a doctor rod, and drying by hanging the sheets in the atmosphere at room temperature. The total coated weight of the resulting stencil sheet ranged from 25.5 to 28 lbs. per 3,000 sq. ft. The thickness of the resulting stencil sheet was about 2¼ mils.

In addition to the listed ingredients, each coating composition included 0.17 gram of an antioxidant per 100 grams of active materials, the antioxidant being Carstab DLTDP, described hereinafter.

Each stencil sheet was assembled with an absorbent sheet for imaging tests. The absorbent sheet was 10 lbs. per 2,880 sq. ft. tissue formed of mixed abaca and wood pulp fibers (Grade 55 tissue, Dexter Corporation). Oil smudging of the image was determined on carbon ribbon copy typed on bond paper, and oil transfer was determined on offset printed stock. Blocking was determined by storing unassembled stencil sheets in contact with each other in foil, at room temperature. Blocking was also determined in most cases by evaluating pinholing upon exposure with a blank sheet of coated paper in a thermal copier. Durability was determined on a label printer type of mimeograph stencil duplicating machine.

Illustrative materials which may be employed in the invention, and referred to herein, are described as follows:

Silica gel

Syloid Al–1 (all Syloids from Davison Div., W. R. Grace Co.) is silica gel having an oil absorption of about 90 lbs./100 lbs. and a particle size range of 1.7–11 microns (90%).

Syloid 162 is silica gel having an oil absorption of about 145 lbs./100 lbs., a particle size range of 1.5–12 microns (90%), and an average particle size of about 7 microns (averages based on the weight of the particles, i.e., approximately one-half by weight above and below the average).

Syloid 255 is silica gel having an oil absorption of about 315 lbs./100 lbs., a particle size range of 0.8–12 microns (90%), and an average particle size of about 3–4 microns.

Syloid 266 is silica gel having an oil absorption of about 310 lbs./100 lbs., a particle size range of 0.6–10 microns (90%), and an average particle size of about 2 microns.

Santocel FR–C (Monsanto Chemical Co.) is a silica gel having an oil absorption of about 350 lbs./100 lbs., and an average particles size of about 5 microns.

Film-forming material

CAB 500–1 is cellulose acetate butyrate grade EAB 500–1 (Eastman Chemical Products) having an average butyryl content of 49.6%, an average acetyl content of 5.5%, a hydroxyl content of 0.15–0.36%, a viscosity of 0.8–1.2 seconds determined by the hereinabove-identified A.S.T.M. method, and a melting point range of about 329–347° F.

CAB 451–1 is cellulose acetate butyrate grade EAB 451–1 (Eastman Chemical Products) having an average butyryl content of 44%, an average acetyl content of 8.5%, an average hydroxyl content of about 1.3%, a viscosity of 1–2 seconds by the A.S.T.M. method, and a melting point range of 302–311° F.

Antioxidant

Carstab DLTDP (Carlisle Chemical Works) is dilauryl thiodipropionate.

Plasticizing material

Mobilsol L (Socony Mobil Oil Co.) is a refined naphthenic petroleum oil having a viscosity of 61 Saybolt Universal Seconds (SUS) at 100° F., an aniline point of 165° F. (straight, A.S.T.M. Test D–1012–62), an API gravity of 25.7°, and a distillation range of 490–708° F. (100%).

Compressor Lube 1500 (Witco Chemical Co.) is a highly paraffinic white mineral oil having typical viscosities of 1537 SUS at 100° F. and 95 SUS at 210° F., and a specific gravity of 0.886. Its aniline point is greater than 230° F. (straight).

Hercolube A (Hercules, Inc.) is the mono-pentaerythritol tetra-ester of caproic acid, having an acid number of 0.1, a saponification number of 420, and a specific gravity of 1.002 at 25° C. Its mixed aniline point is 62° F.

MCP–42 (Mobil Chemical Co.) is a mixed tetra-ester of pentaerythritol and a mixture of aliphatic acids having 5–10 carbon atoms and an average carbon number of 6.9. The acids include 15–20% branched chain and the balance straight chain alkanoic acids. The specific gravity is 1.00 at 25° C. Its mixed aniline point is 42° F.

MCP–99 (Mobil Chemical Co.) is a mixed tri-ester of trimethylol propane and a mixture of aliphatic acids having 5–10 carbon atoms and an average carbon number of 8.3. The acids are straight chain alkanoic acids. The specific gravity is 0.985 at 25° C. Its mixed aniline point is 58° F.

Ucon LB–70–X (Union Carbide) is polypropylene glycol monobutyl ether having a viscosity of 70 centipoises at 100° F. Its mixed aniline point is 77° F.

Ucon LB–300–X (Union Carbide) is polypropylene glycol monobutyl ether having a viscosity of 300 centipoises at 100° F. Its mixed aniline point is 102° F.

Solulan 5 (American Cholesterol Products) is a polyoxyethylene ether of lanolin alcohols and contains lanolin sterols. It is a 5 mole ethylene oxide ether of the lanolin alcohols. It typically has an acid number of 3 max., a hydroxyl number of 120–135, a saponification number of 10 max., and an iodine value of 20–30. Its mixed aniline point is less than 40° F.

Modulan (American Cholesterol Products) is acetylated USP lanolin as described in U.S. Pat. No. 2,725,334. It typically has an acid number of 3 max., a hydroxyl number of 10 max., a saponification number of 95–125, and a melting range of 30–40° C. Its mixed aniline point is 131° F.

Acetulan (American Cholesterol Products) is a liquid fraction of acetylated lanolin alcohols typically having an acid number of 1 max., a hydroxyl number of 8 max., a saponification number of 180–200, an iodine number of 6–10, a specific gravity of 0.850–0.880 at 25° C., and a viscosity of about 10 centipoises at 25° C. Its mixed aniline point is 35° F.

Hercolyn D (Hercules, Inc.) is a hydrogenated methyl ester of rosin purified by steam distillation, a liquid having a Gardner-Holdt viscosity at 25° C. of Z2–Z3 and an acid number of 7. Its mixed aniline point is 58° F.

Abitol (Hercules, Inc.) is technical hydroabietyl alcohol having a viscosity of 200 centipoises at 80° C., a specific gravity of 1.008 at 25° C., a maximum acid number of 0.4, a maximum saponification number of 16, and a mixed aniline point of less than 40° F.

Cellolyn 21 (Hercules, Inc.) is a phthalate ester of technical hydroabietyl alcohol. It typically has an acid number of 8, a saponification number of 129, a specific gravity of 1.05 at 25° C., a softening point (Hercules drop method) of 65° C., and a mixed aniline point of 55° F.

Cellolyn 104 (Hercules, Inc.) is a pentaerythritol ester of rosin, typically having an acid number of 30, a specific gravity of 1.13 at 25° C., a softening point (Hercules drop method) of 101° C., and a mixed aniline point of 145° F.

Staybelite Ester 3 (Hercules, Inc.) is a triethylene glycol ester of hydrogenated rosin, typically having a viscosity of 385 SUS at 100° F., an acid number of 6, a specific gravity of 1.08 at 25° C., and a mixed aniline point of 61° F.

Staybelite Ester 5 (Hercules, Inc.) is a glycerol ester of hydrogenated rosin purified by steam distillation, typically having a softening point (Hercules drop method) of 81° C., an acid number of 5, a specific gravity of 1.06 at 25° C., and a mixed aniline point of 85° F.

Staybelite Resin (Hercules, Inc.) is hydrogenated rosin, typically having a softening point (Hercules drop method) of 75° C., an acid number of 165, a saponification number of 167, a specific gravity of 1.045 at 25° C., and a mixed aniline point of 36° F.

Limed Poly-Pale Resin (Hercules, Inc.) is a reaction product of partially dimerized rosin and hydrated lime containing 5–7% calcium, and typically having a softening point of 175° C. (Hercules drop method), an acid number of 63, a specific gravity of 1.10 at 25° C., and a mixed aniline point of 141° F. The product includes calcium di-resin acid carboxylate, wherein a calcium ion is linked to the carboxyl groups of two resin acid molecules.

Poly-Pale Resin (Hercules, Inc.) is a partially dimerized rosin, typically having a softening point of 102° C. (Hercules drop method), an acid number of 145, a saponification number of 148, and a specific gravity of 1.073 at 25° C.

Flexalyn (Hercules, Inc.) is a diethylene glycol ester of rosin, having a softening point (Hercules drop method) of 44° C., an acid number of 6, a specific gravity of 1.0 at 25° C., and a mixed aniline point of 76° F.

Pexate 510 E (Hercules, Inc.) is a rosin-derived thermoplastic resin containing 10.1% zinc, and typically having a softening point of 118° C., a specific gravity of 1.16 at 25° C., and a mixed aniline point of 109° F. (theor.). The product includes zinc di-resin acid carboxylate, wherein a zinc ion is linked to the carboxyl groups of two resin acid molecules.

Permalyn 330 (Hercules, Inc.) is a glycerol ester of stabilized resin acids, typically having a softening point of 87° C. (Hercules drop method), an acid number of 7, a specific gravity of 1.06 at 25° C., and a mixed aniline point of 67° F. (theor.)

Surfactant AR–150 (Hercules, Inc.) is a medium chain length ethylene oxide adduct of rosin, typically having a viscosity of 400 centipoises at 25° C., and a specific gravity of 1.099 at 25° C.

Halowax 1014 (Koppers Co.) is a mixture of penta- and hexachloronaphthalene having about 62% chlorine, a hard amorphous waxy material typically having a softening point of 137° C., a viscosity of 35 SUS at 150° C., a maximum acid number of 0.05, and a specific gravity of 1.78 at 25° C.

Halowax 1001 (Koppers Co.) is a mixture of tri-and tetrachloronaphthalenes having about 50% chlorine, a hard amorphous waxy material melting to a very mobile liquid at 90–95° C., and having a viscosity of 30 SUS at 130° C., a maximum acid number of 0.05, and a specific gravity of 1.58 at 25° C.

Piccotex 75 (Pennsylvania Industrial Chemical Co.) is a copolymer of vinyl toluene and alpha-methylstyrene, having a softening point of 75° C., an acid number less than 1, a specific gravity of 1.04. at 25° C., and a mixed aniline point of 87° F.

Polyvis O (Cosden Oil and Chemical Co.) is polyisobutylene, an oily liquid having an average molecular weight of about 400, a viscosity of 150 SUS at 100° F. and 42 SUS at 210° F., a specific gravity of 0.837 at 25° C., and an aniline point of 211° F. (straight).

Piccolastic A–50 (Pennylvania Industrial Chemical Co.) is polystyrene having an average molecular weight of 350, a ball and ring melting point of 50° C., and a specific gravity of 1.04 at 25° C.

Piccoumaron 410L (Pennsylvania Industrial Chemical Co.) is a polyindene resin having a softening point of 100° C., a bromine number of 12, a melt viscosity of 100 centipoises at 175° C., and a mixed aniline point of 128° F.

Piccovar 450 (Pennsylvania Industrial Chemical Co.) is an alkyl-aromatic thermoplastic hydrocarbon resin having a large number of cyclic molecular structures. It has a softening point of 100° C., a maximum acid number of 1, a bromine number of 17, a melt viscosity of 100 centipoises at 185° C., a specific gravity of 1.05 at 25° C., and a mixed aniline point of 116° F.

Estynox 408 (Baker Castor Oil Co.) is iso-octyl epoxy stearate. It has an iodine number of 2, a hydroxyl number of 4.8, a saponification number of 138, a specific gravity at 25° C. of 0.92, a viscosity of 18 centistokes at 25° C., and a mixed aniline point of 53° F.

The following examples illustrate stencil sheets having various coating compositions according to the invention. In the examples, the aniline points and viscosities refer to measurements on the plasticizer or mixture of plasticizers, and do not include the film-former, silica gel or

solvents. The volumetric relationships are significant only for the film-forming and plasticizing materials, which constitute the herein-termed active materials, and are calculated only for such materials. It will be understood that the invention is not limited to the examples, which are merely illustrative, or to the materials, proportions, conditions, and procedures set forth therein.

EXAMPLE 1

The following coating composition was deposited on stencil base tissue, providing a total coated weight of about 28 lbs. per 3,000 sq. ft.:

Material	Volume, percent	Parts by weight
CAB 500-1	14.3	16.7
Hercolyn D	21.2	21.6
Hercolube A	25.3	25.3
Cellolyn 21	11.1	11.7
Mobilsol L	28.1	25.0
Syloid 255		4.0

NOTE.—Plasticizer mix: Mixed aniline point, ° F.—95; Viscosity, cps at 77° F.—97.

The Hercolube A in the composition is a low tack material contributing significantly to the lower tack of the plasticizing materials, minimizing blocking. Blocking is improved still further by the Syloid 255. The Cellolyn 21 serves to maintain stencil durability, while also contributing significantly to low oil transfer.

The stencil durability was rated good. The imaging speed, imaging quality, oil smudging, oil transfer, and blocking all were rated very good.

The plasticizing material when tested had a tack index of 11.5. When cooled from a melt, a mixture of the film-forming and plasticizing materials (omitting the Syloid 255) formed an opaque, crumbly gell with no obvious oil separation.

EXAMPLE 2

Coating compositions were prepared containing the following materials:

Material	Volume, percent	Parts by weight
CAB 500-1	14.3	1.67
Hercolube A	25.9	2.58
Staybelite Ester No. 5	25.9	2.74
Mobilsol L	34.0	3.01

NOTE.—Plasticizer mix: Mixed aniline point, ° F.—107; Viscosity, cps at 77° F.—180.

A control composition was prepared, having no silica gel. Compositions containing silica gel were prepared, employing Syloid 255, Syloid 162, Syloid AL-1, or Santocel FR-C, in proportions of ½, 1, 2, 4, 6, 8, 12, 16, and 20 parts by weight (or parts per 100 parts of the above film-forming and plasticizing materials). The compositions were deposited on stencil base tissue to provide total coated stencil weights of about 25–28 lbs. per 3,000 sq. ft., and the stencils were evaluated comparatively.

The control was rated: durability, very good; imaging speed and quality, very good; oil smudging, fair to good; and oil transfer and blocking, fair.

It was found that, in general, silica gel provided improvement over the control in oil rating and/or blocking commencing at about 1 part of silica gel, and such improvement extended to about 20 parts of silica gel.

The high oil absorbing materials, Syloid 255 and Santocel, performed best at the low levels, commencing at 1 part, and imaging speed and quality commenced to fall off at a proportion of about 12 parts. On the other hand, the lowest oil absorbing material, Syloid AL-1, showed less improvement at a proportion of 1 part, and substantially retained durability, imaging speed and imaging quality characteristics while improving oil smudging and blocking at 20 parts. The tests indicated that the durability, imaging speed, and imaging quality of the control were retained with all additives from 2 parts to 8 parts of silica gel, while improving on the control in oil smudging, oil transfer, and blocking, and that blocking was very good with all additives from 2 to 20 parts.

The plasticizing material of the composition had a tack index of 12.4. When cooled from a melt, a mixture of film-forming and plasticizing materials was a viscous slush with small lumps, having no substantial amount of liquid which could be poured from the solid.

EXAMPLE 3

The following coating composition was deposited on tissue to provide a total coated weight of about 28 lbs. per 3,000 sq. ft.:

Material	Volume, percent	Parts by weight
CAB 500-1	14.3	16.9
Hercolube A	31.4	31.7
Abitol	13.4	13.8
Cellolyn 21	5.0	6.6
Mobilsol L	35.9	32.4
Syloid 255		4.0

NOTE.—Plasticizer mix: Mixed aniline point, ° F.—107; Viscosity, cps. at 77° F.—48.

The stencil durability was rated good; the imaging speed, imaging quality, oil smudging, oil transfer and blocking all were rated very good. The Syloid 255 improved the oil transfer and blocking qualities, although imaging speed and quality were slightly lower than without Syloid.

The plasticizing matreial when tested had a tack index of 12.2. When cooled from a melt, a mixture of the film-forming and plasticizing materials was a soft gel.

EXAMPLE 4

The following composition was deposited on tissue to provide a total coated weight of about 26.5 lbs. per 3,000 sq. ft.

Material	Volume, percent	Parts by weight
CAB 500-1	14.3	15.6
Hercolube A	41.0	38.3
Halowax 1014	10.0	16.6
Cellolyn 21	5.0	4.9
Mobilsol L	29.7	24.6
Syloid 255		4.0

NOTE.—Plasticizing materials: Mixed aniline point, ° F.—102; Viscosity, cps. at 77° F.—750.

The stencil durability was rated good; imaging speed very good; imaging quality very good; oil smudging and transfer very good; and blocking very good to exceptional. The Syloid 255 improved the oil transfer and blocking qualities.

The plasticizing materials were mutually soluble at elevated temperatures, but were found to contain undissolved Halowax 1014 at room temperaturee. All plasticizing materials were soluble in the solvent. A coated stencil from which the Syloid was omitted had a white cast apparently due to Halowax 1014 present in excess of its compatibility with the remaining plasticizing materials at room temperature. The performance characteristics indicated that the Halowax 1014 functioned as a plasticizer during imaging while acting at least partially as a filler in the coating composition at room temperature.

EXAMPLE 5

The following composition was deposited on tissue to provide a total coated weight of about 28 lbs. per 3,000 sq. ft.:

Material	Volume, percent	Parts by weight
CAB 500-1	14.3	16.5
Flexalyn	64.0	64.4
Mobilsol L	21.7	19.2
Syloid 255		4.0

NOTE.—Plasticizer mix: Mixed aniline point, ° F.—101; Viscosity cps. at 77° F.—18,250.

The stencil durability was rated exceptional; imaging speed fair to good; imaging quality good; oil smudging very good; oil transfer very good to exceptional; and blocking very good. In the absence of the Syloid 255, blocking was rated poor.

When cooled from a melt, a mixture of the film-forming and plasticizing materials was a slightly sticky, soft wet paste with no pourable liquid. The plasticizing material had a tack index of 7.5. In this example, the Syloid obviated the blocking problem where the tack index was below the minimum value otherwise specified.

EXAMPLE 6

The following coating composition was deposited on tissue to provide a total coated weight of about 27.5 lbs. per 3,000 sq. ft.:

Material	Volume, percent	Parts by weight
CAB 500-1	14.3	16.7
Poly-pale resin	42.85	45.9
Mobilsol L	42.85	38.1
Syloid 255		4.0

NOTE.—Plasticizer mix: Mixed aniline point, ° F.—116.

The stencil durability was rated very good to exceptional; imaging speed very good; imaging quality good; oil smudging and oil transfer exceptional; and blocking good.

When cooled from a melt, a mixture of the film-forming and plasticizing materials formed a mixture of a hard cohesive solid and a liquid, the pourable liquid volume being about ⅔ or greater of the solid volume, substantially greater than specified in the absence of Syloid. Also, the aniline point of the plasticizer mix was above the maximum specified in the absence of Syloid. When the coating composition was employed without Syloid, blocking was rated poor, and oil transfer fair.

The following Examples 7–11 show additional improved coating compositions according to the invention, applied similarly to the preceding examples:

EXAMPLE 7

Material	Composition A		B		C		D	
	Volume, percent	Weight parts	Volume, percent	Weight, parts	Volume, percent	Weight, parts	Volume, percent	Weight parts
Syloid 255		4		6		4		4
CAB 500-1	14.3	16.1	14.3	16.0	14.3	16.7	14.3	16.1
Hercolyn D	24.0	23.6	12.1	11.8	11.2	11.4	21.2	20.8
Hercolube A	24.0	23.1	25.9	24.7	31.4	31.2	25.0	24.1
Cellolyn 21							5.0	5.1
Mobilsol L	18.9	16.2	16.5	14.1	28.1	24.6	28.1	24.1
Pexate 510E	18.9	21.0	18.9	20.9				
Permalyn 330			12.3	12.5				
Staybelite Ester #3					15.0	16.2		
Halowax 1001							6.4	9.8
Plasticizer mix:								
Mixed aniline point, ° F	90	90	90	90	97	97	95	95
Viscosity, cps. at 77° F	500	500			65	65	57	57

EXAMPLE 8

Material	Composition A		B		C		D		E	
	Volume, percent	Weight, parts	Volume, percent	Weight, parts	Volume, percent	Weight, parts	Volume, percent	Weight, parts	Volume, percent	Weight parts
CAB 500-1	14.3	16.7	14.4	17.1	14.3	16.5	14.3	16.6	14.3	16.5
Syloid 255		4		4		4		4		4
Hercolyn D	21.2	21.6			13.4	13.5				
Hercolube A	36.4	36.4	38.5	38.8	12.9	12.7	43.5	43.2	45.7	45.1
Cellolyn 21			11.2	11.9	6.0	6.2				
Mobilsol L	28.1	25.0	35.9	32.2	25.2	22.2	25.0	22.2	20.0	17.6
Piccotex 75					28.2	29.0				
Piccolastic E-50							17.2	18.0		
Piccovar 450									20.0	20.8
Plasticizer mix:										
Mixed aniline point, ° F	96	96	106	106	102	102	100	100	98	98
Viscosity, cps. at 77° F	39	39	49	49	1,980	1,980				

EXAMPLE 9

Material	Composition A Volume, percent	A Weight parts	B Volume, percent	B Weight parts	C Volume, percent	C Weight parts	D Volume, percent	D Weight parts	E Volume, percent	E Weight parts
Syloid 255		4		4		4		4		4
CAB 500-1	14.3	16.8	14.3	16.8	14.3	18.3	15.8	20.3	14.3	18.0
Hercolyn D	57.1	58.4	49.1	50.4						
Hercolube A									20.0	21.5
Mobilsol L			36.6	32.8	47.2	46.1				
Modulan	28.6	24.8								
Tridecyl alcohol					38.5	35.6				
Solulan 5							70.0	66.4		
Compressor lube 1500							14.2	13.3		
Butyl stearate									65.7	60.5
Plasticizer mix:										
Mixed aniline point, ° F.	[1] 82	[1] 82	105	105	95	95	[1] 70	[1] 70	[1] 73	[1] 73
Viscosity, cps. at 77° F.				176					11.5	11.5

[1] Theoretical.

EXAMPLE 10

Material	Composition A Volume, percent	A Weight, parts	B Volume, percent	B Weight, parts	C Volume, percent	C Weight, parts	D Volume, percent	D Weight, parts	E Volume, percent	E Weight, parts
Syloid 255		4		4		4		4		4
CAB 500-1	14.3	17	14.3	17	14.3	18.8	14.3	17.0		
CAB 451-1									14.3	16.6
Hercolube A									85.7	83.6
Ucon LB-70-X	85.7	83								
Ucon LB-300-X			85.7	83						
Hexadecyl alcohol					85.7	81.2				
Castor oil							85.7	83		
Plasticizer:										
Mixed aniline point, ° F.	77	77	102	102	70	70	90	90	62	62
Viscosity cps. at 77° F.	20	20			40	40	720	720		

EXAMPLE 11

Material	Composition A Volume, percent	A Weight, parts	B Volume, percent	B Weight, parts	C Volume, percent	C Weight, parts
Syloid 255		4		4		4
CAB 500-1	14.3	18.4	14.3	16.8	14.3	16.9
Hercolyn D			21.2	21.4		
Hercolube A			14.7	14.8	31.4	31.6
Cellolyn 21			7.0	7.3	5.0	5.2
Mobilsol L			28.1	25.2	28.1	25.2
Solulan 5	85.7	81.6				
MCP-42			14.7	14.3		
MCP-99					21.2	21.1
Plasticizer mix:						
Mixed aniline point, ° F.	<40	<40	104	104	100	100
Viscosity, cps. at 77° F.			67	67	32	32

Other representative materials that may be employed similarly to Hercolube A, MCP-42, and MCP-99 in the foregoing examples include the mono-pentaerythritol tetra-ester of valeric acid; the 89% mono-pentaerythritol, 11% di-pentaerythritol tetra-ester of caproic acid; the 89% mono-pentaerythritol, 11% di-pentaerythritol tetra-ester of caprylic acid; and the di-pentaerythritol tetra-ester of caproic acid, in the same order of preference. Additional materials that may be similarly employed include trimethylol propane tripelargonate, mixed mono- and di-pentaerythritol tetra-esters of mixed C-7, C-8, and C-10 alkanoic acids, and mixed mono- and di-pentaerythritol tetracaprylate.

We claim:

1. A thermographic stencil sheet which comprises an ink-impervious base sheet, and an ink-impervious coating thereon of a heat-flowable composition of

(a) a resinous thermoplastic film-forming material comprising cellulose acetate butyrate,

(b) an oily, substantially non-volatile plasticizing material, said plasticizing material being partially but incompletely compatible with said film-forming material, the amount of (a) being about 8–50% by weight based on the total amount of (a) plus (b), and

(c) a finely divided silica gel having an oil absorption capacity of at least about 90 lbs./100 lbs. and present in a proportion of about 1–20% by weight of said film-forming and plasticizing materials,

said film-forming and plasticizing materials forming a clear homogeneous single phase melt when heated and forming a solid-liquid two-phase mixture when cooled from the melt to room temperature, said film-forming and plasticizing materials having a minimum compatibility temperature of about 120° F., at least one phase of said mixture incorporating substantial proportions of both said film-forming material and said plasticizing material,

said film-forming and plasticizing materials being soluble in a volatile solvent and forming a substantially homogeneous continuous imperforate coating when deposited from a solution thereof, and said coating being provided on said base sheet by deposition of said composition on the base sheet from a solvent solution thereof containing said silica gel in dispersion and removing solvent therefrom, the melting point of said coating being at least about 150° F., said coating further becoming flowable and irreversibly physically altered when heated to its melting point for forming ink permeable image areas in the cooled stencil sheet.

2. A stencil sheet as defined in claim 1 wherein said silica gel has a maximum average partice size of about 10 microns.

3. A stencil sheet as defined in claim 2 wherein at least about 90% by weight of the particles of said silica gel are in the range of about 0.5–12 microns.

4. A stencil sheet as defined in claim 1 wherein said plasticizing material comprises a member selected from the group consisting of mineral oil, castor oil, hexadecyl alcohol, polypropylene glycol monobutyl ether, polyoxyethylene ethers of lanolin alcohols, pentaerythritol tetra-esters of aliphatic acids having from 5 to 10 carbon atoms, and trimethylol propane tri-esters of aliphatic acids having from 5 to 10 carbon atoms.

5. A stencil sheet as defined in claim 4 containing in a proportion by weight of said film-forming and plasticizing materials, about 5–85% of said member selected from said group.

6. A stencil sheet as defined in claim 5 wherein said silica gel has an oil absorption capacity above about 300 lbs./100 lbs. and is present in a proportion of about 2–12% by weight of said film-forming and plasticizing materials.

7. In a method of making an imaged stencil sheet employing a thermographic stencil sheet which includes an ink-impervious layer of a heat-flowable composition, wherein image areas of the stencil sheet are subjected to heat generated in adjacent image areas of an original by infrared ray absorption to render the composition flowable in the stencil sheet image areas and the composition is caused to flow therefrom and thereby form corresponding ink-transmitting image openings in the stencil sheet, the improvement which comprises employing as said stencil sheet the stencil sheet of claim 1.

8. A thermographic stencil sheet which comprises an ink-pervious base sheet, and an ink-impervious coating thereon of a heat-flowable composition of

(a) a resinous thermoplastic film-forming material comprising cellulose acetate butyrate,

(b) an oily, substantially non-volatile plasticizing material having a tack index of at least about 10, and a maximum mixed aniline point of about 110° F., said plasticizing material being partially but incompletely compatible with said film-forming material, the amount of (a) being about 8–50% by weight based on the total amount of (a) plus (b), and

(c) a finely divided silica gel having an oil absorption capacity of at least about 90 lbs./100 lbs. and present in a proportion of about 1–20% by weight of said film-forming and plasticizing materials,

said film-forming and plasticizing materials forming a clear homogeneous single phase melt when heated and forming a solid-liquid two-phase mixture when cooled from the melt to room temperature, said film-forming and plasticizing materials having a minimum compatibility temperature of about 120° F., at least one phase of said mixture incorporating substantial proportions of both said film-forming material and said plasticizing material,

said mixture having a maximum pourable liquid volume of about one-fourth the volume of the solid phase,

said film-forming and plasticizing materials being soluble in a voltatile solvent and forming a substantially homogeneous continuous imperforate coating when deposited from a solution thereof, and said coating being provided on said base sheet by deposition of said composition on the base sheet from a solvent solution thereof containing said silica gel in dispersion and removing solvent therefrom, the melting point of said coating being at least about 150° F., said coating further becoming flowable and irreversibly physically altered when heated to its melting point for forming ink permeable image areas in the cooled stencil sheet.

9. A stencil sheet as defined in claim 8 wherein said silica gel has a maximum average particle size of about 10 microns.

10. A stencil sheet as defined in claim 9 wherein said silica gel has an oil absorption capacity above about 300 lbs./100 lbs. and is present in a proportion of about 2–12% by weight of said film-forming and plasticizing materials.

11. A stencil sheet as defined in claim 10 wherein said plasticizing material comprises a member selected from the group consisting of mineral oil, castor oil, hexadecyl alcohol, polypropylene glycol monobutyl ether, polyoxethylene ethers of lanolin alcohols, pentaerythritol tetra-esters of aliphatic acids having from 5 to 10 carbon atoms, and trimethylol propane tri-esters of aliphatic acids having from 5 to 10 carbon atoms, said member selected from said group being present in a proportion of about 5–85% by weight of said film-forming and plasticizing materials.

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MURRAY KATZ, Primary Examiner

U.S. Cl. X.R.

117—157; 106—189, 191; 250—65 T

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,694,244 Dated SEPTEMBER 26, 1972

Inventor(s) Larson, Leonard G., Anderson, Bror E., and Schick, Margery L.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 23: Change "vimage" to -- image --

6, 72: Change "steroils" to -- sterols --

13, Example 2: In the table, under "Parts by Weight" heading, change the listed values as follows:

"1.67" to -- 16.7 --

"2.58" to -- 25.8 --

"2.74" to -- 27.4 --

"3.01" to -- 30.1 --

Signed and sealed this 10th day of April 1973.

(SEAL)
Attest;

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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