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J. R. HEFFNER

3,228,327

MULTIPURPOSE DUPLICATING MASTER

Filed April 5, 1962

2 Sheets-Sheet 1



FIGURE 1

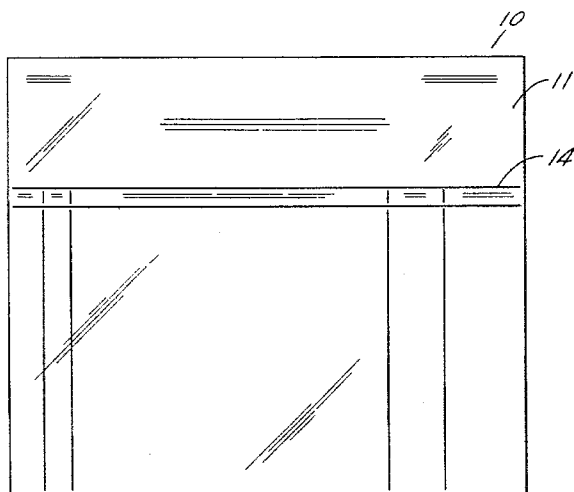


FIGURE 2

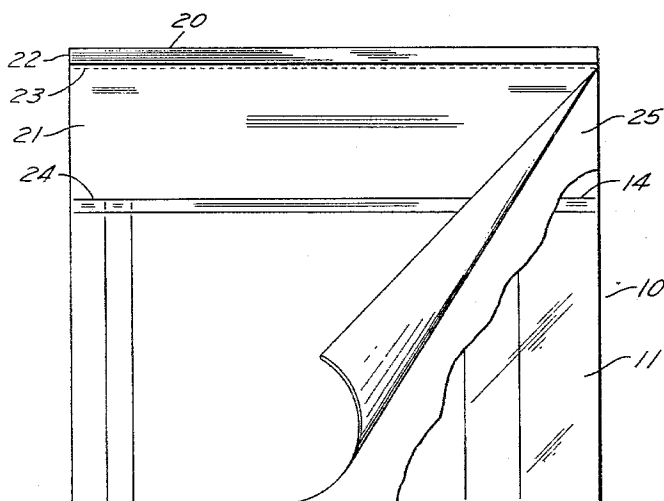


FIGURE 3

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3,228,327

2 Sheets-Sheet 2

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1

2

3,228,327

MULTIPURPOSE DUPLICATING MASTER

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12 Claims. (Cl. 101—149.2)

The present invention relates to coating compositions, sheet material of a particular type coated with the particular coating compositions, duplicating masters made from such sheet material, and padded forms embodying such masters. The invention more particularly relates to certain coating compositions and sheet materials coated therewith, and to duplicating masters made therefrom which have desirable and advantageous characteristics not hitherto possessed by known duplicating masters, or sheet materials from which they have been made.

It is known in the art to reproduce printed, typed, or written matter from one sheet to another by various processes, including reproductive procedures of the offset or lithographic printing type, such as commonly employed using paper masters to produce copies on ordinary paper or so-called "second generation" masters for use in further reproductions by the same process, or by differential light transmission-absorption procedures involving the differential transmission of light of various wavelengths through a master to be copied and onto or into a second sheet containing materials reactive to said wavelengths to produce indicia thereon and thereby provide duplicates or negatives of the sheet being copied, such as the diazo, photographic, or like processes, or involving the employment of differential transmission or absorption of light wavelengths in the infra-red or heat-producing range, rather than the ultra-violet, to produce images and duplicates by means of a sheet sensitized to infra-red rays and/or heat, or involving utilization of electrostatic phenomena. Each of these processes of reproduction has met with success, in view of the ever increasing requirement for copies and more particularly exact duplicate copies according to business practices of today. The several processes have attained wide acceptance not only in separate fields of utilization, but also in overlapping areas, and in some areas due to efficient marketing practices all three types of reproduction are employed, although by no means uniformly. Thus, for example, in the freight-transfer industry, where the use of masters of the type concerned in the present invention and forms containing the same is a uniform business control practice, all three of the aforementioned types of reproductive processes are presently in use, some firms employing one method of reproduction and other firms employing another. However, since the several duplicating procedures involve considerably different mechanisms, equipment of different design and nature is required for the employment or application of the different processes. This heterogeneous disposition of the various equipment for reproduction throughout the industry has resulted in widespread delay and confusion, since it is uneconomic for every office to be equipped with all three types of reproducing apparatus, although at any time any office may be called upon to reproduce copies from masters which are adapted for use with but one type of reproducing apparatus. It is apparent that, aside from the uneconomic possibility of equipping each office with all types of equipment, the answer is to provide a multi-purpose master which is adapted for use in any of the various reproductive processes with its particular type of equipment.

To state the obvious solution to this problem, however, is only to present an entirely new project with many additional problems. For use in offset printing or lithography,

a master must be adapted to receive ink and repel water in certain areas and to receive water and repel ink in other areas. It must therefore possess a desirable balance of hydrophilic and oleophilic properties, as well as a requisite degree of wet tensile strength. For use in differential light transmission-absorption types of reproductive processes, a master must possess transparency or permeability so as to allow penetration of the particular wavelength of light necessary to effect the reproductive color-forming reaction in the sensitized sheet adapted to respond to the differential impact of such rays. The combination of requisite characteristics for the various types of reproducing masters has not previously been available in any one master or in any one sheet material from which such a master might be formed, especially since the surface of such sheet material or master formed therefrom must, for such multi-purpose adaptability, also be receptive to a retentative of the different types of printing, typing, or writing media variously required for reproduction according to the several processes. As is well known, all of the processes will not reproduce all of the printing, typing, writing, or like media available, or even the media required for reproduction according to other of the several processes of reproduction. The few types of multi-purpose masters which have hitherto been available and utilizable for duplication according to more than one of the several types of processes have all been attended by difficulties, such as lack of sufficient transparency, so that a master which was utilizable in offset printing procedures, where utilizable at all in other types of duplicating procedures was not sufficiently effective to allow reproduction at a commercially acceptable rate. Conversely, masters utilizable in differential light transmission-absorption types of processes have been notorious for their inadequacies when an attempt was made to employ same in offset printing or lithography. For example, one problem inherent in the production of a master utilizable in both offset and differential light transmission-absorption reproduction processes is that it must not only be sufficiently transparent and/or penetrable to allow transmission thereto and/or therethrough of light rays differentially in the one type of process, but it must also have a sufficiently retentive surface so that media printed, typed or written thereon adheres sufficiently to the surface thereof and is not readily washed off during the process of lithographing or offset reproduction. Thus media retentiveness is a factor which must be considered in addition to the hydrophilic-oleophilic balance and the characteristic of wet tensile strength requisite for offset or lithographic masters. The provision of all such characteristics in one sheet material and a master produced therefrom, as well as the requisite degree of transparency necessary for the differential light transmission-absorption processes, has obviously presented a serious problem which has not been solved up to the present time. Provision of such a sheet material having the necessary characteristics to allow its employment in a duplicating master for use in all of the aforementioned types of duplicating processes, masters produced therefrom, and forms embodying such masters, would obviously be of considerable economic significance. Likewise, provision of duplicating masters utilizable in all of the various aforesaid reproducing procedures at rapid and economically feasible rates would be of considerable importance.

It is accordingly an object of the present invention to provide novel coating compositions, sheet material coated therewith, duplicating masters produced from such sheet material and adapted for multi-purpose use, and forms embodying such masters.

An additional object of the invention is the provision of duplicating masters which are utilizable in and repro-

duceable by offset procedure and which are moreover utilizable as masters for reproduction by the various other processes hereinbefore mentioned at rapid and economically feasible rates.

A further object of the invention is the provision of a sheet material or master which may be employed in the production of a "second generation" master by the offset process, which "second generation" master may then serve as master in any of the aforementioned reproductive processes of either the offset or the differential light transmission-absorption type.

Other objects of the invention will be apparent to one skilled in the art and still other objects of the invention will become apparent hereinafter.

In accord with the present invention, the foregoing and additional objects have been accomplished by the provision of certain novel coating compositions, sheet material coated therewith, duplicating masters thereof, and forms including such masters. The starting sheet material coated according to the invention has particular requisite characteristics and the coating composition involved, which is applied to at least one surface of the sheet material, is in itself a particular combination of at least two and preferably three different reactants, each having definite prerequisites, in definite proportions.

The invention is further illustrated by the drawings, in which:

FIGURE 1 is an edge view of a duplicating master produced from a relatively transparent sheet of paper uniformly coated on at least one surface thereof in accord with the present invention;

FIGURE 2 is a top plan view of the duplicating master shown in FIGURE 1; and

FIGURE 3 is a top plan view of a padded form embodying the duplicating master shown in FIGURE 2, with overlying sheets partially turned back and cut away to reveal the duplicating master.

FIGURE 4 is a graph illustrating the composition ranges of the three binary coating compositions of the invention (lines A, A' and A'') and the ternary coating composition of the invention (line B), as well as the optimum composition ranges for the preferred ternary coating composition of the invention (line C).

The types of starting sheet material which may be employed in the production of the coated sheet and masters made therefrom according to the present invention are those sheet materials permitting a minimum ultraviolet light penetration of twenty-five (25) percent and preferably in excess of forty (40) percent, as compared with air, using an ultraviolet beam having a peak of about 3650 Angstrom units, as transmitted through Corning filter No. 5860 (or Photovolt No. 5162) as determined with a photoelectric transmission densometer (Photovolt No. 5012). Included in such types of sheet material may be mentioned any base sheet stock of paper or other material such as regenerated cellulose, cellulose acetate, or other papers and sheet materials of such requisite degree of ultraviolet transmission, including for example the type of paper known as "greaseproof" paper, which is made from highly hydrated machine calendered pulp according to procedure well known in the art, or glassine papers of various types (which are supercalendered greaseproof papers), or other papers transparentized in the usual manner, according to procedure customarily employed in the paper industry, before application of the coating composition, in each case with or without surface pretreatment which does not materially alter the transparency of the sheet material for purposes of making the same more receptive to the coating composition of the present invention. An especially preferred starting sheet material is parchmentized paper, especially 25 to 50 pound per 3000 square feet parchmentized paper, such as commonly produced in the paper industry using concentrated sulphuric acid and as more recently known also produceable using concentrated ortho-phosphoric acid. The additional

characteristics requisite in such starting sheet material to be coated are that it should have, in addition to the minimum degree of ultraviolet transmission, a minimum wet tensile strength of two (2) pounds per inch (machine direction) as determined by TAPPI test method T 456 m-49. Since the coating composition used in the invention is transparent, it is only necessary to provide such starting sheet material as has the aforementioned characteristics, and then to coat such sheet material uniformly, thereby to impart to at least one surface thereof the characteristics of hydrophilic-oleophilic balance and ink retentiveness afforded by the present invention.

While some of these starting papers or sheet materials, such as parchment, are not only transparent but can also be used as an offset master, without modification, when so employed they still leave much to be desired in view of their characteristic pick up of ink in the non-printed background areas and corresponding lack of contrast in and legibility of the finished reproduced product. Also, whereas various papers and other sheet materials have already been coated with numerous coating materials, including polyvinyl alcohol and the like, the coating material of the present invention involves a particular combination of specific ingredients in particular proportions, which appear to be critical for attainment of the desired results.

The transparent or substantially transparent coating compositions of the invention may be formed from any one or more of the following combinations:

I. Binary

- (a) polyvinyl alcohol having certain prerequisites and dialdehyde starch, also having certain prerequisites.
- (b) polyvinyl alcohol having certain prerequisites and a silicon oxide, also having certain prerequisites.
- (c) a silicon oxide having certain prerequisites and dialdehyde starch, also having certain prerequisites.

Preferably, however, the composition is formed from the following combination:

II. Ternary

- (d) polyvinyl alcohol, and dialdehyde starch and a silicon oxide, all having particular prerequisites.

Mixtures of the binary systems may also be employed, the resulting composition of course being a ternary composition.

The prerequisites of the respective ingredients are as follows:

Polyvinyl alcohol.—The polyvinyl alcohol employed has at least ninety-five (95) percent and preferably a higher percentage of its existing hydroxyl groups present as free unesterified hydroxyl groups, preferably even as high as 99% or higher, that is, as close to 100% as possible. Such materials are commercially available and in most cases, due to their method of production, will contain acetate groups to the extent that hydroxyl groups therein are still esterified. Such materials are, for example, presently available under the "Evanol" (Du Pont) trademark. Polyvinyl alcohols of the stated prerequisite hydroxyl content having a viscosity (4% solution in water at 20° C. determined by Hoesppler falling ball method) in centipoises of 4-6, 23-28, 28-32, 45-55 and 55-65, have all been found operative.

Dialdehyde starch.—The dialdehyde starch employed is disclosed in U.S. Patents 2,648,629 and 2,713,553, is starch containing polymeric 2,3-dialdehyde derived therefrom by oxidation to the extent of at least about fifty percent aldehyde content, usually at least about 75% and preferably above 90% aldehyde content. Such materials are also commercially available in the form of dialdehyde starch having 2,3-dialdehyde content within the ranges indicated, especially under the trademark "Sumstar." Reference is made to the publication entitled "Sumstar Dialdehyde Starch," Technical Bulletin No. 6-129, published by Miles Chemical Company, Elkhart, Indiana (Copyright 1959).

Silicon oxide.—The prerequisites of the silicon oxide is

that it be a solid hydrophilic water-insoluble silicon oxide having an average particle size of two microns or less, usually less than .05 micron, and preferably between about .015 and .02 micron, as measured on its largest particle diameter, and a refractive index (n_D^{20}) not greater than 1.6. Any silicon oxide of these properties is operative. The silicon oxide is preferably isotropic, by which is meant that the material is optically homogeneous, having only one index of refraction. A characteristic and preferred silicon oxide is the colloidal silica (silicon dioxide) prepared in hot gaseous environment by vapor-phase hydrolysis having an average particle size of 0.015–0.02 micron, an external surface area of about 175–225 square meters per gram, and about 99.9% silicon dioxide content on a moisture-free basis, such as that sold under the trademark "CAB-O-SIL" by Cabot Corporation, Boston 10, Mass.

The operative ranges of ingredients for the coating compositions or systems identified above are as follows, the total number of parts of the stated ingredients being 100:

Table I

Silicon oxide	PVA	Dialdehyde starch (DAS)
(a) from 0..... to 0..... Preferred: 0.....	97.6..... 50..... 60 up.....	2.4..... 50..... 40 or less.
(b) from 3..... to 95..... Preferred: 55 or less.....	97..... 5..... 45 up.....	0..... 0..... 0.....
(c) from 95..... to 30..... Preferred: 40 up.....	0..... 0..... 0.....	5..... 70..... 60 or less.
(d) .1 to 95..... Preferred: .1 to 65.....	.1 to 97.6..... 15 to 97.5.....	.1 to 72..... .1 to 55.....

In preparing the preformed coating compositions of the invention, the following procedure is employed.

When polyvinyl alcohol is used as one ingredient of the composition, the polyvinyl alcohol is in any event placed in solution in a volatile, non-reactive solvent, usually an aqueous, preferably water, solution. When dialdehyde starch is a second ingredient of the composition, this is also placed in the same type solvent. When both polyvinyl alcohol and dialdehyde starch are employed as ingredients of the composition, their respective solutions are combined, preferably by adding the dialdehyde starch solution to the polyvinyl alcohol solution. In the event silicon oxide is to be a second or third ingredient of the composition, this may be combined with either of the solutions or with the combined polyvinyl alcohol-dialdehyde starch solution. The silicon oxide when to be present in the combination may be added in either the dry state or as an aqueous slurry, preferably as a slurry in water. Combination of the ingredients into solutions or suspensions containing preselected quantities of the same produces a final coating composition having the predetermined ratio and amounts of the components. Although in some cases heating of the solvent and polyvinyl alcohol to a temperature as high as 195–205 degrees Fahrenheit is advantageous in effecting solution of the polyvinyl alcohol, and although the solvent and contained dialdehyde starch is frequently heated to a temperature as high as 160 degrees Fahrenheit to effect its solution, care should be exercised that the dialdehyde starch is not heated substantially above 200 degrees Fahrenheit, either alone or in combination, for prolonged periods.

The ratios of polyvinyl alcohol and dialdehyde starch which have been found suitable for preparation of binary coating compositions according to the invention are as indicated in the foregoing Table I, with a ratio of about ten parts of polyvinyl alcohol to one part of dialdehyde starch being optimum, especially when starch containing above about 90% of the 2,3-dialdehyde and polyvinyl alcohol containing at least about 99% unesterified free

hydroxyl groups are employed. At the higher ratios of polyvinyl alcohol to dialdehyde starch, polyvinyl alcohol having a lower percentage but still in excess of 95% free unesterified hydroxyl groups may be employed, while at the lower ratios of polyvinyl alcohol to dialdehyde starch, starch having a lower percentage but still in excess of 50% dialdehyde content may be employed. Likewise, while adequate hydrophilic-oleophilic balance and satisfactory freedom from tendency to wash is obtained using polyvinyl alcohol having a high degree, nearly 100%, of free unesterified hydroxyl groups and dialdehyde starch having a lesser percentage but always at least 50% 2,3-dialdehyde content, or employing polyvinyl alcohol having a lesser percentage but always 95% or greater free unesterified hydroxyl groups and dialdehyde starch having a high 2,3-dialdehyde content of about 90% or above, the optimum hydrophilic-oleophilic balance appears to be effected at between a three:two and a fifty:one ratio, preferably at about a ten to one ratio, of polyvinyl alcohol having about 99% free unesterified hydroxyl groups and dialdehyde starch having at least about 90% 2,3-dialdehyde content.

By way of illustration, using the PVA and DAS and the binary composition as representative, polyvinyl alcohol and dialdehyde starch may be mixed together in the proper ratios and applied to the sheet material to be coated in the form of a solution or dispersion of the resulting product. At least a part and usually all of the product is in solution. The polyvinyl alcohol is usually placed in solution, the starch having the requisite dialdehyde content is placed in solution, and the latter solution added to the former. Other orders of admixing the reactants may be employed. The solvent employed for the components may be any nonreactive volatile solvent which may be evaporated from the surface of the sheet material after coating to provide a uniform layer of the dialdehyde starch-polyvinyl alcohol composition on the surface of the sheet material treated. A preferred solvent for obtaining the desired solution of the polyvinyl alcohol and the dialdehyde starch is water, with or without minor amounts of alcohols, dioxane, plasticizers or the like, although any other nonreactive volatile solvent which dissolves the components and will volatilize upon standing in dry air or upon the application of heat may be employed. When the dialdehyde starch does not go readily into solution, a solubilizing agent such as sodium acetate, sodium bisulfite, disodium phosphate, borax, or the like, in amount of about one to five parts per hundred parts of solvent, may be employed. Solution of the dialdehyde-starch is ordinarily readily obtained by slight heating as to about 140–160 degrees Fahrenheit and agitation of the mixture of dialdehyde starch and solvent. Rapid solution of the polyvinyl alcohol may be readily effected according to conventional procedure. According to a preferred procedure, separate solutions of polyvinyl alcohol and dialdehyde-starch are prepared and admixed and the mixture thereafter agitated, although slight heating as to about 140–160 degrees Fahrenheit may also be employed to effect a more rapid solution, which is ordinarily complete in thirty to sixty minutes or so. Setting of the composition on the sheet material is effected during the subsequent drying or heating to volatilize the solvent.

After the two solutions are admixed, or when the ingredients are combined together in any other manner to provide a solution of the components, it is only necessary to provide sufficient of a uniform coating of the composition on the surface of the starting sheet material to attain at least a five (5) pound per inch (machine direction) wet tensile strength (TAPPI T 456 m-49) of the coated sheet material when the starting sheet material has less than this requisite strength to begin, and this may be accomplished in conventional surface-coating manner by the employment of a coating head such as a roll coater, a trailing blade or an air brush, or on a size

press, all as commonly employed for surface coating. When coating compositions of the invention containing combinations of ingredients other than PVA and DAS, or additional ingredients, are prepared and employed, the procedure is substantially the same, in accord with the more general procedural directions already given.

The total solids in the coating compositions of the invention, prior to being coated upon the base sheet material, may vary over a wide range. For example, concentrations of total solids from one percent to about sixty percent are operative, with from about three percent to about fifteen percent being preferred for ordinary high-speed coating methods. The amount of total solids in the composition may be advantageously increased in some cases, as when thinner starting sheet materials are employed. In other cases, more than one coating may be applied, although this is not preferred for reasons of economy. The concentration of total solids in the coating composition is only limited by the highest concentration which may be conveniently handled using available coating equipment at economical coating speeds. In some applications it is advantageous to employ a plurality of coatings, as in cases where a more uniform coating is desired, in which cases double coating heads may be employed, with or without drying in between. Although both sides of a base sheet material may be coated at the same time, as in a size press, it is sometimes advantageous to coat the sides individually, and this may be conveniently accomplished for example by individual passes with a trailing blade coating head.

The total solids coated on the base sheet material in this manner should be in the range of 0.1 to thirty pounds per ream (3,000 square feet) per side of base sheet material, whether coated on one or both sides, and the preferred range is from 0.2 to five pounds total solids per ream (3,000 square feet) per side of base material, again whether coated on one or both sides. The concentrations of the coating compositions employed to obtain this desired result are never less in total solids content than the desired total solids content desired to be obtained on the base sheet material by a single application and the exact solids concentration of the composition will depend upon various factors such as the method of application, the rate of application, and whether one or more coating applications are to be made on the surface of the base sheet material.

In the event it is desired to produce the coated sheet materials of the invention otherwise than by employment of a preformed coating composition, this may for example be accomplished by minor procedural variation, as by coating the sheet material with the polyvinyl alcohol in solution, allowing the coating to partially dry, gel, or set, and then overcoating with dialdehyde starch solution, if desired containing the silicon oxide. This is productive of a coating having the requisite characteristics and relative ratios of ingredients, providing only that the amounts of solids in each of the several solutions be pre-selected in accord with the ranges previously stated. Similarly, when polyvinyl alcohol and silicon oxide are to be used in a binary system, or when dialdehyde starch and silicon oxide are to be used in a binary system, the same procedure may be employed, with the initial coating in each case being with the polyvinyl alcohol, when present in the composition, or with the dialdehyde starch solution, when present in the composition.

For final production of the coated sheet material, the sheet, already coated as above described, is dried as in heated dry air, on steam-heated rollers, with a gas flame, or combinations thereof, preferably at incremental temperatures, during which drying the setting of the transparent coating composition on the sheet material is completed. The coated sheet may if desired be supercalendered to improve its surface and provide better ink lay, to decrease caliper and thereby also improve transparency, and to generally improve its appearance, although

supercalendering has not been found necessary to provide a suitable coated sheet material product for use in accord with the present invention. The coated sheet material may finally be stored or cut into sheets of suitable dimensions. Inasmuch as the coating compositions when set on the base sheet material are transparent, the minimum total solids content of 0.1 to thirty, preferably 0.2 to five, pounds of total solids per 3000 square foot ream per side of sheet material, the minimum wet tensile strength of five pounds per inch (machine direction) by TAPPI tests T456 m-49, and the same minimum ultraviolet transmission properties set forth above for the starting sheet material (namely at least 25% and preferably at least 50% as compared with air), are all characteristics of the coated sheet material of the invention.

In the preparation of masters, the coated sheet material is either first printed as desired and then cut or alternatively cut to desired dimensions and then printed, but preferably the former, all according to conventional procedure in the printing and business forms producing industry. The text and/or vertically and/or horizontally arranged lines and/or columns may be printed on the master in any desirable or convenient manner, again as conventional in the art. The medium for such printing of the master, however, should be such as will reproduce according to any of the several methods of reproduction, if it is desired that such printed material shall reproduce along with added material. The printed form may in some cases be printed with media which is non-reproductive in any of the various reproducing processes mentioned, although just the reverse is preferred. For certain applications, it is acceptable that the master have no printing whatever thereon, as in those cases where only the printed, typed, or written material subsequently added is desired to be reproduced. In practice, the masters may be directly extended, i.e., printed, typed, or written upon, with many of the usual printing, typing or writing media, selected for their ability to reproduce in the several processes of interest, whereafter reproductions can be run off from the master which as indicated is thus made directly by inscribing or imprinting reproducing indicia upon the face thereof, rather than indirectly by means of an adjacent carbon sheet, as in a pad. Alternatively, reproducing indicia may be placed upon the master indirectly, as by means of carbon paper or a pigment-coated transfer sheet.

In the preparation of forms embodying the duplicating masters, sheets are cut from usual paper stock of the type employed in composing such forms, printed with the usual text material and/or vertically and/or horizontally disposed lines and/or columns, and arranged together with the duplicating master which may also be, and which preferably is, imprinted or inscribed with the identical text and arrangement of lines and columns as is provided on the other sheets of paper from which the completed form is to be composed. Sheets of carbon paper, preferably a hard carbon type, of the same dimensions are disposed between the various sheets of printed forms and between a sheet of printed form and the master. A backing sheet of heavier weight may or may not be provided. The sheets are usually so arranged that printing, typing or writing on the uppermost sheet produces an impression on all of the underlying sheets so as to transfer an image of the added printed, typed or written material to all of the underlying non-carbon sheets and to the master. The so-arranged sheets are glued at their upper edges, or such edges may be glue dipped so as to provide a pad of sheets secured together at its upper edge. A perforation line is ordinarily provided in spaced parallel relation to the glued edge, for rapid and convenient disassembly of the pad into its individual sheet components. In some embodiments, while arranged together in pads, the sheets are not secured together, but may merely be placed underlying

each other and held in place, or for instance so arranged in a ring or other binder.

Referring now to the drawings for a more complete understanding of the invention, FIGURE 1 is an edge view of a duplicating master 10 produced from a sheet of relatively transparent paper coated in accord with the present invention. FIGURE 1 shows paper sheet 12 and the coating composition layer 11 on the upper surface thereof. The broken lines indicate a coating composition layer 13 which may be present on the under surface of said paper sheet, and the presence of which coating layer 13 constitutes a preferred embodiment of the invention.

FIGURE 2 shows a plan view of a duplicating master 10, the edge view of which is shown in FIGURE 1. The coating layer 11 is shown facing the viewer. Various arranged printed text and horizontally and vertically disposed lines are provided on the surface of the sheet, as at 14. The printed text and horizontally and vertically arranged lines 14 either may or may not be in ink of a reproducing nature according to one or more of the various processes of reproduction, but are preferably reproducible by all processes.

FIGURE 3 shows a plan view of a padded form 20 in accord with the invention, embodying master 10. Padded form 20 includes the usual relatively light-weight top paper sheet, as commonly employed in the business forms industry, having text material and vertically and horizontally arranged lines printed upon the surface thereof, as at 24. Carbon paper sheet 25 of common hard carbon type is interposed between upper paper sheet 21 and master 10, having coating layer 11 upwardly disposed. Printed text and vertically and horizontally arranged lines 14 on coating layer 11 of master 10 are in registry with printed text and vertically and horizontally arranged lines 24 on top paper sheet 21. The various sheets 21, 25, and 10 comprising padded form 20 are joined at their top edges as by gluing so as to constitute them into an assembled pad 20 until tear strip 22, to which the sheets are all integrally joined along perforation line 23, is removed, thereby severing the padded form 20 into its individual sheet components. To the extent of the registry of printed text and lines 14 and 24, respectively, provided on coated surface 11 of master 10 and on sheet 21, the filling in of blanks or the addition of textual material on sheet 21 will provide a master 10 which is an exact duplicate of top sheet 21, due to the carbon sheet 25 disposed therebetween.

Referring now to FIGURE 4, there is shown a composition diagram for the various coating compositions of the present invention. The lines designated A, A' and A'' define the ranges for the three binary coating compositions of the invention, while the area enclosed within the line designated B defines the composition ranges for the preferred ternary coating composition of the invention. A single diagram is used for convenience of illustration, it being understood that as shown for the ternary system line B cannot be zero at any point. Line C encloses the optimum ranges for the ternary system. As will be seen from FIGURE 4, the composition may contain only two components or three components. The ranges of the components as shown in FIGURE 4 are identical with those set forth in Table I hereof. The optimum ranges for the preferred ternary coating composition of the invention, as seen from FIGURE 4, are from 0.1 to 55 parts of dialdehyde starch, from 15 to 97.5 parts of polyvinyl alcohol, and from 0.1 to 65 parts of silicon oxide, the total number of parts being 100, so that the figures not only express parts per 100 but also weight percent. Within the optimum ranges for the ternary composition (line C) all of the advantages set forth previously for the present invention are uniformly obtained, as within this area a superior balance of offset properties are procured without detriment to

the properties required for other reproduction processes. In the area bounded by the line designated B, the ranges are from 0.1 to 72 parts of dialdehyde starch, from 0.1 to 97.6 parts of polyvinyl alcohol, and from 0.1 to 95 parts of silicon oxide, per 100 parts of composition, and within these ranges the ternary composition is characterized by a balance of desirable properties which is superior to that exhibited by any of the various binary compositions of the invention. As will be seen from FIGURE 4, in area "a" the adhesion of reproductive media to the sheet material becomes a problem, whereas in area "b" excessive ink receptivity is encountered, and in area "c" excessive water sensitivity, which also results in wash-off of the media such as ink from the master, is experienced. In area "a," the problem is due to lack of anchorage rather than water sensitivity.

The following examples are given by way of illustration only and are not to be construed as limiting.

Example 1.—Binary—PVA+DAS

A solution was prepared by adding three parts of polyvinyl alcohol (Evanol 72-60; 55-65 c.p.s. viscosity, 99-100% free hydroxyl groups) to 97 parts of water and agitating for five to ten minutes. Heat was applied until a temperature of 195 to 205° Fahrenheit was attained and this temperature was maintained until solution was complete. In various runs, the time required for complete solution was usually thirty to sixty minutes.

A dialdehyde starch solution was prepared using 100 parts of water in which one part of sodium acetate was dissolved. This solution was heated to 160° Fahrenheit, agitated constantly, and ten parts of 90% oxidized dialdehyde starch (i.e., starch having a starch 2,3-dialdehyde content of at least 90%) (Sumstar S or 190A) was added slowly so that uniform wetting occurred. Agitation was continued at 160° Fahrenheit for thirty minutes.

After cooling the polyvinyl alcohol solution to room temperature, sufficient of the 90% oxidized dialdehyde starch solution was added thereto so as to give a ratio of ninety parts of PVA to ten parts of DAS. After thoroughly mixing, the solution was applied to 28 lb./ream parchment paper by means of a size press.

Drying and setting of the coating on the parchment was accomplished using a gas flame and regular steam-heated dryer drums with incremental heating of the rolls from 190° F. to 240° F. The transparently-coated stock was supercalendered to improve smoothness of surface for better ink lay, to decrease caliper and increase transparency, and to improve appearance.

Some of the stock was cut into 8½ x 11 inch grain long sheets, which were then imaged upon so as to provide an arrangement of lines of the nature shown in FIGURE 2 hereof. These sheets were now masters.

Duplication using these masters was effected using three different offset duplicating machines including two different types, viz., Davidson Model 241 and Addressograph-Multigraph Model 1250, in each of the three cases using the particular etching solution and fountain solution provided for normal use with the machine in question. Results from all three offset duplicators was very satisfactory for 20-30 copies, with excellent reproduction of second generation masters, which in turn gave excellent reproduction when they were tested as masters.

Diazo reproduction using the masters of either first or second generation was excellent at speeds of 21 to 24 ft./min. on an Ozalid diazo reproduction machine Model OM-16.

Reproduction using the masters on a standard Thermo-fax machine Model 17J gave excellent copies.

Example 2.—Binary—PVA+Silicon Oxide

A PVA solution was prepared from the same ingredients and in the same manner as given in Example 1. An amount of colloidal silica having an average particle size between 0.015 and 0.02 micron, a surface area of about 175-225 square meters per gram, an n_D^{20} of 1.55, and a

99.9% silicon dioxide content on a dry basis was added to equal the weight of the polyvinyl alcohol in the solution, thereby giving a 1:1 weight ratio (50 parts to 50 parts). Application, setting, and testing were accomplished in the same manner as given in Example 1. The reproduction test results using the master thus produced were equal to those indicated in Example 1.

Example 3.—Binary—Silicon Oxide+DAS

Dialdehyde starch (90% oxidized) solution was produced as in Example 1 and diluted to a three percent by weight solution by addition of water. To this solution was added with stirring colloidal silica (having an average particle size between 0.015 and 0.02 micron, a surface area of about 175–225 square meters per gram, an n_D^{20} of 1.46, and a 99.9% silicon dioxide content on a dry basis) in an amount equal to that of the dialdehyde starch, so that a 1:1 weight ratio of silica to dialdehyde starch existed (50 parts to 50 parts). Application, setting, and testing were accomplished in the same manner as given in Example 1. The reproduction test results using the master thus produced were equal to those indicated in Example 1.

Example 4.—Ternary—PVA, DAS and Silicon Oxide

Ten parts of PVA (99–100% of free hydroxyl groups) were added to 100 parts of water and the mixture was agitated for ten minutes. Heat was applied until a temperature of 195 to 205° F. was reached and this temperature was maintained until solution was complete, which usually required 30–60 minutes.

A solution of dialdehyde starch (90% oxidized) was prepared as described in Example 1.

After the polyvinyl alcohol solution had cooled, dialdehyde starch solution was added thereto and the solutions thoroughly admixed. The quantities were selected to provide two parts of dialdehyde starch to one part of polyvinyl alcohol in the solution. Thus, after addition, the product was a three percent PVA and six percent dialdehyde starch solution. Colloidal silica (having an average particle size between 0.015 and 0.02 micron, a surface area of about 175–225 square meters per gram, an n_D^{20} of 1.46, and a 99.9% silicon dioxide content on a dry basis) was added, in an amount equal to the weight of the polyvinyl alcohol present, so that 50 parts of dialdehyde starch were present for each 25 parts of PVA and each 25 parts of silicon oxide.

The coating composition was applied by size press to a 28 pound parchment paper. Drying and setting of the coating was effected with steam-heated dryer drums. The transparently-coated stock was supercalendered to improve sheet appearance, to improve smoothness for better ink lay, and to decrease caliper for better ultra-violet light transmission. In this case, "supering" was done on a small hand supercalender.

Both "supered" and "non-supered" sheets were converted to imaged masters as in Example 1 and tested on the three separate offset duplication machines using each machine's own etching solution and fountain solution, just as in Example 1. All masters tested produced at least 20 excellent copies, as well as excellent second generation masters, which in turn produced excellent copies.

Diazo reproduction from the masters was excellent using speeds from 21 to 24 ft./min. on an Ozalid diazo machine Model OM-16.

Thermofax reproduction on a Model 17J Thermofax machine was also excellent.

Example 5.—Ternary—Variation

Six parts of PVA (99–100% free hydroxyl groups) was added to 94 parts of water and solution effected as in Example 1. Dialdehyde starch (90% oxidized) solution was also prepared as given in Example 1. The dialdehyde starch solution was added to the PVA solution, the quantities being selected so that forty parts of PVA to one part of dialdehyde starch was present. Colloidal silica (having an average particle size between 0.015 and 0.02 micron, a surface area of about 175–225 square meters per gram,

an n_D^{20} of 1.46, and a 99.9% silicon dioxide content on a dry basis) in an amount equal to the amount of PVA, or six parts of silica, was dispensed in 94 parts of water, and the slurry added to the PVA–DAS solution. After mixing thoroughly, a ratio of 49.4 parts of PVA to 49.4 parts of silicon oxide to 1.2 parts of dialdehyde starch was present in the composition.

Application, setting, and testing were completed as in Example 4. The results were identical to those reported in Example 4.

Example 6.—Ternary—Variation

The procedure of Example 5 was repeated except that silica in an amount equal to two-thirds the weight of PVA was added to give a ratio of 40 parts of PVA to 27 parts of silicon oxide to 1 part of dialdehyde starch, or 1.4 parts of dialdehyde starch to 59.5 parts of PVA to 39.1 parts of silicon oxide per 100 parts.

Application, setting, and testing was as given in Example 4. The results were the same as given in Example 4.

Example 7.

Additional binary compositions were made up in accord with Examples 1 through 3 and additional ternary compositions were made up in accord with Examples 4 through 6. These were coated upon base sheet materials of suitable characteristics in accord with the preceding examples. In each case, the relative amounts of the ingredients in either the binary or ternary systems were in accord with the graph of FIGURE 4 and in accord with Table I hereof. In each case of the binary system composition and the sheet material coated therewith, a satisfactory result was obtained. The masters produced from this binary composition coated sheet material were found to be suitable in the same manner as the products of Examples 1 through 3.

When a ternary composition was used for coating of the base sheet material stock, the results were in accord with those given in Examples 4 through 6, in each case the results on the various types of duplicating or reproduction equipment being excellent. In addition, the reproductive characteristics of the master were subject to less variation from run to run than observed when using masters produced from sheet materials coated with the binary compositions.

Although the coating compositions of the invention have been particularly described with reference to the coating of a base sheet material having certain ultraviolet transmission characteristics and when applied to such base sheet material produce an excellent coated sheet suitable for use as a master in reproduction according to all of the various types of processes previously described, it is to be understood that the coating compositions of the invention may also be employed or applied in the coating of an opaque sheet material or a sheet material not having the particular desirable ultraviolet transmission characteristics previously set forth. Such coated sheet materials are nevertheless of value as masters in reproduction processes which do not require ultraviolet transmission, such as offset lithography, heat absorption processes, electrostatic processes, and the like.

It is to be understood that various substitutions of equivalents will be apparent to one skilled in the art, and that various modifications and alterations may be made in the process, compositions, and products of the present invention without departing from the spirit or scope thereof, wherefore the present invention is limited only by the scope of the appended claims.

I claim:

1. A duplicating master adapted for use in duplicating processes of either the offset or the differential light transmission-absorption type, comprising a base sheet material of parchmentized paper having at least one surface thereof uniformly coated with a material comprising, per 100 parts of the stated ingredients, polyvinyl alcohol (PVA) and dialdehyde starch (DAS) in relative pro-

portions of 50 to 97.6 parts of PVA to 50 to 2.4 parts of DAS, the starting PVA being characterized by having at least about ninety-five (95) percent of its existing hydroxyl groups present as free unesterified hydroxyl groups, the starting DAS being characterized by containing at least about fifty (50) percent of starch 2,3-dialdehyde, the said coating being substantially transparent when set on the surface of the base sheet material employed, the coated sheet material having at least a five (5) pound per inch (machine direction) wet tensile strength as tested according to TAPPI Test T 456 m-49, a minimum degree of ultraviolet transmission of at least twenty-five (25) percent as compared with air using an ultraviolet beam having a peak at about 3650 Angstrom units, as transmitted through a Corning filter No. 5860 and determined with a photoelectric transmission densometer (Photovolt No. 5012), and the total solids coated on the base sheet material being in the range of 0.1 to 30 pounds per 3,000 square foot ream per side of base sheet material.

2. A duplicating master adapted for use in duplicating processes of either the offset or the differential light transmission-absorption type, comprising a sheet material of claim 1 having indicia upon the coated surface thereof in a medium reproductive in both offset and differential light transmission-absorption types of reproduction processes.

3. A duplicating master adapted for use in duplicating processes of either the offset or the differential light transmission-absorption type, comprising a base sheet material having at least one surface thereof uniformly coated with a material comprising, per 100 parts of the stated ingredients, polyvinyl alcohol (PVA) and dialdehyde starch (DAS) in relative proportions of 50 to 97.6 parts of PVA to 50 to 2.4 parts of DAS, the starting PVA being characterized by having at least about ninety-five (95) percent of its existing hydroxyl groups present as free unesterified hydroxyl groups, the starting DAS being characterized by containing at least about fifty (50) percent of starch 2,3-dialdehyde, the said coating being substantially transparent when set on the surface of the base sheet material employed, the coated sheet material having at least a five (5) pound per inch (machine direction) wet tensile strength as tested according to TAPPI Test T 456 m-49, a minimum degree of ultraviolet transmission of at least twenty-five (25) percent as compared with air using an ultraviolet beam having a peak at about 3650 Angstrom units, as transmitted through a Corning filter No. 5860 and determined with a photoelectric transmission densometer (Photovolt No. 5012), and the total solids coated on the base sheet material being in the range of 0.1 to 30 pounds per 3,000 square foot ream per side of base sheet material.

4. A duplicating master according to claim 3, wherein the starting PVA is at least about 99% hydrolyzed and the starting DAS contains at least about 75% of starch 2,3-dialdehyde.

5. A duplicating master according to claim 3, wherein the starting DAS contains at least about 90% starch 2,3-dialdehyde.

6. A duplicating master according to claim 3, wherein the weight ratio of PVA to DAS is about ten to one.

7. A duplicating master according to claim 3, wherein the base sheet material is about 28 to 50 pounds per 3,000 square foot ream parchmentized paper.

8. A duplicating master according to claim 7, having a minimum ultraviolet light penetration of at least about

40% as compared with air using an ultraviolet beam having a peak at about 3650 Angstrom units as transmitted through a Corning filter No. 5860, as determined with a photoelectric transmission densometer (Photovolt No. 5012).

9. A duplicating master adapted for use in duplicating processes of either the offset or the differential light transmission-absorption type, comprising a sheet material of claim 3 having indicia upon the coated surface thereof in a medium reproductive in both offset and differential light transmission-absorption types of reproduction processes.

10. A duplicating master adapted for use in duplicating processes of either the offset or the differential light transmission-absorption type, comprising a base sheet material having at least one surface thereof uniformly coated with a material comprising, per 100 parts of coating composition, polyvinyl alcohol (PVA) and dialdehyde starch (DAS) in relative proportions of 0.1 to 97.6 parts of PVA to 0.1 to 72 parts of DAS, the starting PVA being characterized by having at least about ninety-five (95) percent of its existing hydroxyl groups present as free unesterified hydroxyl groups, the starting DAS being characterized by containing at least about fifty (50) percent of starch 2,3-dialdehyde, said coating material additionally containing about 0.1 to about 95 parts per 100 parts of coating composition of a particular mineral consisting essentially of silicon dioxide having an average particle size not greater than two (2) microns and refractive index ($n_D^{20\text{ }^\circ\text{C}}$) not greater than 1.6, the said coating being substantially transparent when set on the surface of the base sheet material employed, the coated sheet material having at least a five (5) pound per inch (machine direction) wet tensile strength as tested according to TAPPI Test T 456 m-49, a minimum degree of ultraviolet transmission of at least twenty-five (25) percent as compared with air using an ultraviolet beam having a peak at about 3650 Angstrom units, as transmitted through a Corning filter No. 5860 and determined with a photoelectric transmission densometer (Photovolt No. 5012), and the total solids coated on the base sheet material being in the range of 0.1 to 30 pounds per 3,000 square foot ream per side of base sheet material.

11. A duplicating master according to claim 10 wherein the coating composition comprises from about 15 to 97.5 parts of PVA, from 0.1 to about 65 parts of said silicon dioxide, and from 0.1 to about 55 parts of DAS.

12. A duplicating master according to claim 10, wherein the starting PVA is at least about 99% hydrolyzed, the starting DAS contains at least about 75% of starch 2,3-dialdehyde, and the silicon dioxide has an average particle size less than .05 micron.

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