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(54) PRODUCING MANIFOLD CARBONLESS FORMS

(71) We, THE MEAD CORPORATION, a corporation organised and existing under the laws of the State of Ohio, United States of America, formerly of Talbott Tower, Dayton, Ohio 45401, United States of America, and now of Mead World Headquarters, Courthouse Plaza, Northeast, Dayton, Ohio 45463, United States of America do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to pressure sensitive copying systems, and more particularly to a process for the production of a manifold carbonless form and to the carbonless form itself.

Manifold forms for commercial and private use have been in common use for several years. Historically, the standard business form has taken a variety of shapes. The most common is a multiple part form with sheets of carbon paper being insertable between the various sheets. This concept is very cumbersome as the carbon paper had to be both inserted, removed and disposed of in addition to the deficiencies commonly noted in the use of carbon paper such as smudging. In response to the obvious problems a form was developed having the carbon paper already inserted between the various sheets making up the form and being available for easy removal and disposal. This removal and disposal was made even more convenient by the attachment of the carbon paper together at one edge, generally the bottom, so that by merely ripping out the bottommost edge of the form all of the carbon paper would be removed. This system has been and still is being used by many retail department stores. All of these systems have historically suffered from one common deficiency, namely the use of carbon paper. Carbon paper, while adequate for some image transfer purposes is not a preferred product as it is very cumbersome to work with, it is very messy and in general does not form the quality image which is desired. In addition, as is commonly encountered with the use of carbon paper the more sheets of carbon paper that are used the fainter the image on the last sheets of the form. This is especially true where more than three to four sheets per form are used. Examples of patent proposals relating generally to the use and manufacture of carbon paper and other image transfer systems containing dyes and pigments include

U.S. Patent 2,299,694 (1942) to Green
U.S. Patent 2,374,862 (1945) to Green
U.S. Patent 3,016,308 (1962) to Macauley
U.S. Patent 3,020,170 (1962) to Macauley
U.S. Patent 3,079,351 (1963) to Staneslow et al

In recognition of the deficiences of carbon paper as an image transfer media a variety of new products have been introduced into the marketplace. One such product is commonly referred to as carbonless paper. Carbonless paper, briefly stated, is a standard type of paper wherein during manufacture the backside of the paper substrate is coated with what is referred to as a CB coating, the CB coating containing one or more colour precursors generally in capsular form. At the same time the front side of the paper substrate is coated during manufacture with what is referred to as a CF coating, which contains one or more colour developers. Both the colour precursor and the colour developer remain in the coating compositions on the respective back and front surfaces of the paper in colourless form. This is true until the CB and CF coatings are brought into abutting relationship and sufficient pressure, as by a typewriter, is applied to rupture the CB coating to release the colour precursor. At this time the colour precursor contacts the CF coating and reacts with the colour developer therein to form an image. Thus the image from the top sheet is transferred to the next sheet without the use of carbon paper. Carbonless paper has proved to be an exceptionally valuable image transfer media for a variety of reasons only one of which is the fact that until a CB coating is placed next to a CF coating both the CB and the CF substrates are in an inactive state as the co-reactive elements are not in contact with one another. Patent proposals relating to carbonless paper products include:

U.S. Patent 2,712,507 (1955) to Green
U.S. Patent 2,730,456 (1956) to Green et al

A third generation product which is in an advanced stage of development and commercialization at this time and which is available in some business sectors is referred to as self-contained paper. Very generally stated self-contained paper refers to an image transfer system wherein only one side of the paper needs to be coated and the one coating contains both the colour precursor, generally in encapsulated form, and the colour developer. Thus when pressure is applied, again as by a typewriter or other writing instrument, the colour precursor capsule is ruptured and reacts with the surrounding colour developer to form an image. Both the carbonless paper image transfer system and the self-contained transfer system have been the subject of a great deal of patent activity. A typical autogeneous record material system, earlier sometimes referred to as "self-contained" because all elements for making a mark are in a single sheet, is disclosed in U.S. Patent 2,730,457 (1956) to Green.

As will be explained in detail below, in an especially preferred arrangement in accordance with this invention, the manifold paper product is produced continuously without requiring roll storage or the like. As can be appreciated from the above the continuous production of a manifold paper product would require simultaneous coating, simultaneous drying, simultaneous printing, and simultaneous collating and finishing of a plurality of paper substrates. Because of the complexities of the drying step this has not been commercially possible to date. More particularly, the drying step involving solvent evaporation and/or water evaporation and the input of heat does not permit the simultaneous or continuous commercial manufacture of manifold forms.

A disadvantage of coated paper products such as carbonless and self-contained stems from the necessity of applying a liquid coating composition containing the colour forming ingredients during the manufacturing process. In the application of such coatings, heretofore, volatile solvents are sometimes used which then in turn require evaporation of excess solvent to dry the coating thus producing voltatile solvent vapours. An alternative method of coating involves the application of the colour forming ingredients in an aqueous slurry, again requiring removal of excess water by drying. Both methods suffer from serious disadvantages. In particular the solvent coating method necessarily involves the production of generally volatile solvent vapours creating both a health and a fire hazard in the surrounding environment. In addition, when using an aqueous solvent system the water must be evaporated which involves the expenditure of significant amounts of energy. Further, the necessity of a drying step requires the use of complex and expensive apparatus to continuously dry a substrate which has been coated with an aqueous coating compound. A separate but related problem involves the disposal of polluted water. The application of heat not only is expensive, making the total paper manufacturing operation less cost effective, but also is potentially damaging to the colour forming ingredients which are generally coated on to the paper substrate during manufacture. High degrees of temperature in the drying step require specific formulation of wall-forming compounds which permit the use of excess heat. The problems encountered in the actual coating step are generally attributable to the necessity for a heated drying step following the coating operation.

The drying step involving solvent evaporation and/or water evaporation and the input of heat does not permit the most economic and efficient manufacture of manifold forms. In addition to the drying step which hinders manifold form production the necessity for the application of heat for solvent evaporation is a serious disadvantage since aqueous and other liquid coatings require that special grades of generally more expensive paper be employed and even these often result in buckling, distortion or warping of the paper since water and other liquids tend to strike through or penetrate the paper substrate. Additionally, aqueous coatings and some solvent coatings are generally not suitable for spot application or application to limited areas of one side of a sheet of paper. They are generally suitable only for application to the entire surface area of a sheet to produce a continuous coating.

Patent proposals considered to have some relevance to this concept include:

canadian Patent 945,443 (1974) to Busch.

U.S. Patent 3,914,511 (1975) to Vassiliades

Another problem which has been commonly encountered in attempts to continuously manufacture manifold forms has been the fact that a paper manufacturer must design paper from a strength and durability standpoint to be adequate for use in a large variety of printing and finishing machines. This requires a paper manufacturer to evaluate the coating apparatus of the forms manufacturers he supplies in order that the paper can be designed to accommodate the requirements of the apparatus and process exhibiting the most demanding conditions. Because of this, a higher long wood fibre to short wood fibre ratio must be used by the paper manufacturer than is necessary for most coating, printing or finishing machines in order to achieve a proper high level of strength in his finished paper product. This makes the final sheet product more expensive as the long fibre is generally more expensive than a short fibre. In essence, the separation of paper manufacturer from forms manufacturer, which is now common, requires that the paper manufacturer overdesign his final product for a variety of machines, instead of specifically designing the paper product for known machine conditions.

By combining the manufacturing, printing and finishing operations into a single manufacturing facility a number of advantages are achieved. First, the paper can be made using ground wood and a lower long fibre to short fibre ratio as was developed *supra*. This is a cost and potentially a quality improvement in the final paper product. A second advantage which can be derived from a combination of manufacturing, printing and finishing is that wast or re-cycled paper hereinafter sometimes referred to as "broke" can be used in the manufacture of the paper since the quality of the paper is not of an overdesigned high standard. Third and most importantly, several steps in the normal process of the manufacture of forms can be completely eliminated. Specifically drying steps can be eliminated by using a non-aqueous, solvent-free coating system and in addition several warehousing and shipping steps can be avoided thus resulting in a more cost efficient product.

Additionally, by using appropriate coating methods, namely non-aqueous, solvent-free coating compositions and methods, and by combining the necessary manufacturing and printing steps, spot printing and spot coating can be realized. Both of these represent a significant cost saving but nevertheless one which is not generally available when aqueous or solvent coatings are used or where the manufacture, printing and finishing of paper are performed at geographically separated manufacturing facilities. An additional advantage of the use of solvent-free, non-aqueous coating compositions and the combination of paper manufacturer, printer and finisher is that when the option of printing followed by coating is available significant cost advantages occur. More particularly, by printing prior to coating from about 10% to about 30% fewer capsulated colour forming ingredients need to be used to achieve the same satisfactory levels of image transferability. This advantage is realized because when the paper is transferred to a forms manufacturer in coated form the paper of necessity will lose some of its capsulated colour formers when printed because of the pressure rupturability of the material. This disadvantage is eliminated when the paper is printed first followed by coating.

Many of the particular advantages of the specific processes and products in accordance with this invention which are described hereinafter are derived from the fact that a non-aqueous, solvent-free coating composition is used to coat the paper substrate. This is in contrast to the coatings used by the prior art which have generally required an aqueous or solvent coating. For purposes of this application the term "100% solids coating" will sometimes be used to describe the coating operation and should be understood to refer to the fact that a non-aqueous, solvent-free coating composition is used and therefore the normal drying step normally present in the manufacture of paper and in coating has been eliminated.

In accordance with a first aspect of this invention, there is provided a process for the production of a manifold carbonless form, comprising: providing a plurality of continuous webs; advancing each web of said plurality of continuous webs at substantially the same speed, said plurality of continuous webs being spaced apart and being advanced in a cooperating relationship with one another; marking at least one web of said plurality of continuous webs with a pattern; applying at least one non-aqueous, solvent-free coating of chromogenic material (as herein defined) to at least a portion of at least one web of said plurality of continuous webs; setting said coating; collating said plurality of continuous webs; and placing said collated continuous webs in contiguous relationship to one another to create a manifold form. The invention also extends to the resultant product.

In a second and alternative aspect of this invention, there is provided a process for the production of a manifold carbonless form, comprising: providing a continuous web;

marking at least one surface of said continuous web with a pattern; applying at least one non-aqueous, solvent-free coating of chromogenic material (as herein defined) to at least a portion of at least one surface of said continuous web; setting said coating to form a marked, coated continuous web; combining said marked, coated continuous web with at least one additional continuous web to form a plurality of continuous webs, each of said additional continuous webs having at least a portion of at least one surface thereof coated with at least one non-aqueous, solvent-free coating of chromogenic material (as herein defined), said coatings being set; collating said plurality of coated continuous webs; and placing said collated continuous webs in contiguous relationship to one another to create a manifold carbonless form. Again, the invention extends to the resultant product.

We shall explain below how the complete production of manifold carbonless forms can be achieved at a single processing or manufacturing facility. The term "carbonless" as used herein shall be understood to be a generic term to encompass any type of image transfer paper or paper system not requiring the use of carbon paper. The carbonless paper will be described herein as having a topmost and bottommost surface corresponding to those surfaces as they would appear to a person using the paper. One, both or none of the surfaces of the carbonless paper can be coated with a chromogenic material. The chromogenic material may be in the form of microcapsules, droplets or other vehicle dispersed in a binder. We also refer below to chromogenic materials which are not capsular. Preferably when the chromogenic material is capsular it is microencapsulated. Included in the term "chromogenic materials" as used herein are colour precursors, colour developers, colour inhibitors and like materials and combinations thereof.

The manifold carbonless forms will usually comprise from 2 to 10 individual sheets and preferably from 2 to 4 individual sheets per form. The actual number of sheets or layers making up the particular carbonless form is not limiting to the practice of our processes, but rather can be manufactured to the convenience of the individual customer.

The apparatus which can be used in our processes includes apparatus which is traditionally used in paper manufacturing and forms printing. During the collating and/or finishing steps, as various continuous webs are advanced towards their final finishing or packing station they must be advanced at substantially the same speed and other process variables must be specifically controlled. For example, if the individual paper webs are various colours indicating second or third copies the collating must be coordinated so that the colours of the forms are properly arranged. Additionally, it is preferred although not essential that the size of the individual continuous webs be substantially equal. It is necessary in the manufacture of carbonless paper forms that the CB/CF coatings be adjacent to one another; and finally it is necessary that the distinction be made between carbonless and self-contained so that two sides coated with a self-contained coating composition are not adjacent to each other. For purposes of this application the arranging of the various sheets in the proper order shall be sometimes referred to as collating the sheets, webs or substrates.

The continuous webs, sometimes referred to herein as substrates, are any of those commonly used in the manufacture of carbonless papers. Included in the preferred continuous web materials are paper and plastics although other substrates can be substituted. The continuous webs can be supplied in any of a variety of shapes, sizes and configurations. The preferred and most common shape is in a roll form. While the particular dimensions of the roll are not critical a standard roll would be sized at approximately a width of from 3 inches to 72 inches and a total length of approximately from 500 feet to 10,000 yards. This particular size has been found suitable to fit more printing and coating apparatus. In this fasion a substrate is printed and coated and then stored for future use in combination with other compatible printed and coated substrates to make a finished manifold carbonless form. After the individual treated substrates have been stored they are placed in collating and finishing apparatus to complete the manufacturing process. In an alternative arrangement the continuous web can be supplied as an on-line substrate forming process. In this particular arrangement the manifold carbonless form manufacturing process is the final stage in the paper making process.

The preferred continuous web material is paper and as developed *supra* the overall quality of the paper can be somewhat lower than was previously considered acceptable and as a result the paper can generally be made using some ground woods and additionally the paper has a lower long fibre to short fibre ratio. This cost saving advantage of lower overall paper quality is realized because the paper can be manufactured specifically for use in combination with known coating and printing apparatus.

A particular advantage enjoyed by our processes is the fact that the printing or marking operation can be completed prior to the coating step. In this fashion it can be seen that fewer encapsulated materials need be coated on the paper; as the from 10% to 30% of the encapsulated material which would normally be ruptured or otherwise destroyed during the printing operation is not necessary as the web has already been printed during the coating operation. This is in contrast to what was previously possible due to the fact that formerly after any coating step a drying step was of necessity required, the drying step generally requiring the application of substantial heat and the expenditure of a significant amount of energy. This represents a substantial cost and convenience advantage over any methods shown or disclosed by the prior art.

As described above in the preferred process the individual substrates are subjected to a printing or marking step prior to the coating step. While this is preferred it is not critical. For purposes of this application the term "marking" shall be used and shall be understood to be generic to printing, writing, lining or any other marking of a continuous web whether the marking is visible or not. In the preferred process the topmost surface of each individual web of the plurality of continuous webs is marked with a printing ink to provide the printed information and blanks usually found in a business form. However, it is sometimes the case that only one surface, normally the topmost surface, of the topmost continuous web will be so marked. The actual content of the marking and the number of webs which are marked are dependent on the particular form being manufactured and may be conveniently adjusted during the manufacturing operation.

In the preferred arrangement the marking step is performed by the application of a marking fluid, preferably a printing ink, by suitable printing apparatus to one or more surfaces of the continuous webs. The preferred printing method is offset although any of the other well known printing methods are equally applicable. The actual printing method is merely an apparatus limitation and depends on the printer capabilities of the particular manufacturer. The inks which can be used in this printing step are any of the inks commonly used in the printing industry today. The ink must only be selected from a group or type the members of which are compatible with the coating process and composition.

For the production of manifold carbonless forms by our process it is necessary that at least one coating composition be applied to at least one surface of at least one continuous web prior to collating into a manifold form. In the preferred arrangement each continuous web of the plurality of continuous webs, except the topmost web, will have a CF coating containing a colour developer on the topmost surface and a CB coating containing an encapsulated colour precursor on the bottommost surface As another preferred arrangement a self-contained image transfer system can be used wherein both the colour developer and colour precursor are coated on a single surface, preferably the topmost surface, of each continuous web again with the exception of the topmost web which does not require any coating material regardless of what particular form of carbonless transfer system is used.

Depending on the particular coating method and composition the coating of a self-contained composition on to the continuous web can require either one or two separate coating steps. While the coating step can be performed by a variety of known methods the preferred coating methods and coating compositions are hot melt suspension media and radiation curable resins. One of the particularly significant advantages found in both of these preferred coating methods is that no coating drying step is necessary. Rather, a curing or setting step is substituted for the drying step and no heat, elapsed time or elevated temperatures are necessary. Thus the coating compositions for use in the process of this invention are best described as solvent-free, non-aqueous coating compositions or expressed differently "100% solids coatings".

HOT MELT SYSTEM

The first preferred coating method involves the use of a hot melt suspension medium, preferably waxes, resins or the like in combination with chromogenic material. This method is particularly suitable when the chromogenic material comprises microcapsules containing a colour precursor or colour precursor combination. The most preferred hot melt suspending media comprise the low molecular weight polar waxes. The hot melt suspending medium procedure described herein will be hereinafter sometimes referred to as the hot melt activation system. The hot melt activation system has been found most suitable for use as the CB coating for carbonless paper although to a somewhat lesser extent it can also function as the CF coating when the chromogenic material suitably comprises a colour developer or colour developer combination. The preferred procedure involves micro-encapsulating a colour precursor or colour developer using any of a variety of well-known microencapsulation techniques most of which require the use of a cross-linking agent with a wall forming compound to initiate an interfacial reaction resulting in the formation of microcapsules having characteristics determined by the particular wall forming compound.

The chromogenic coating composition for use in the hot melt embodiment will usually comprise a dispersion of a chromogenic material in a hot melt system. The chromogenic material can be either soluble or insoluble in the hot melt system and the colour precursors are preferably in microencapsulated or dispersed form. Filler materials can also be added to the hot melt to modify the properties of the final coated substrate. The use of solvents, which require heat to remove them during the setting of the coated film, is avoided.

The chromogenic colour precursors we have found most useful in the practise of the hot melt embodiment are the electron-donors and include the lactone phthalides, such as crystal violet lactone, and 3,3-bis-(1′-ethyl-2 -methylindol- 3′-yl) phthalide, the lactone fluorans, such as 2-dibenzylamino -6-diethylaminofluoran and 6-diethylamino -1,3-dimethylfluorans, the lactone xanthenes, the leucoauramines, the 2-(omega substituted vinylene)-3,3- disubstituted-3-H indoles and 1,3,3- trialkylindolinospirans. Mixtures of these colour precursors can be used if desired. In the preferred hot melt process microencapsulated oil solutions of colour precursors are used. The colour precursors are preferably present in such oil solutions in an amount of from 0.5% to 20.% based on the weight of the oil solution, and the most preferred range is from 2% to 7%.

The hot melt suspending media we have found generally useful include waxes and resins. The preferred group of compounds we have found useful as hot melt suspending media include: deresinated, oxidized mineral waxes such as the montan waxes; amide waxes such as bis-stearamide wax, stearamide wax, and behenamide wax; fatty acid waxes; hydroxylated fatty acid waxes; hydroxy stearate waxes; oxazoline waxes; amine waxes; and mixtures thereof. The hot melt suspending medium is preferably characterized by having a penetration hardness of less than or equal to from 0.1 to 20, a melting point of from 60°C to 140°C, a narrow melting range, a low viscosity when molten, a certain amount of polarity and a light colour. Any wax or wax mixture with the foregoing properties can, we believe, be used successfully as suspending media in practice. These waxes are all suitable to act as a dispersing medium for the chromogenic material and other ingredients of the coating composition and at the same time are compatible with the chromogenic properties of the chromogenic material. These materials are settable to a solid when cooled.

Included in the preferred group of hot melt suspending media are the following waxes: 2-n-heptadecyl -4,4-bis-hydroxy -methyl-2-oxazoline, N,N′- ethylenebisstearamide, N-(2-hydroxyethyl) -12-hydroxystearamide, glyceryl monohydroxystearate and ethylene glycol monohydroxystearate.

Other waxes of this type which we have generally proved to be effective are generically described as the modified mineral type, synthetic waxes or those of vegetable origin or combinations thereof. These waxes are suitably characterized by a high melting point and a great hardness which eliminates wax transfer to the developing sheet, thus improving image clarity, increasing blocking temperature and diminishing packing problems. One of the most preferred group of waxes is the deresinated crude montan waxes. These waxes are produced from a raw material of bitumen-rich lignite which is extracted with organic solvents to form a crude montan wax. The montan wax is deresinated by extraction with organic solvents followed by oxidation with chromic acid to yield acid waxes.

Another type of preferred hot melt suspending medium is a non-polar hydrocarbon wax, such as Be Square 170/175 (m.p. range 170-175°F) from Bareco Division of Petrolite Corporation which includes a small amount of dispersing agent. The dispersing agent may, for instance, be Turkey Red Oil.

The preferred waxes have a penetration hardness of from 0.1 to 20 measured by the needle penetration test given a ASTM designation of D1321-61T. We have found the range of 0.1 to 20 to represent a practical penetration hardness range. A more preferred range is from 0.1 to 3 and the most preferred range is from 0.1 to 1 on the same needle penetration index. The needle penetration index covers a test procedure for the empirical estimation of the consistency of waxes derived from petroleum by measurement of the extent of penetration of a standard needle. This method is applicable to waxes having penetration of not greater than 250. The penetration of petroleum wax is the depth, in tenths of a millimetre, to which a standard needle penetrates into the particular wax under defined conditions. The defined conditions generally are that the sample is melted, heated to 30°F above its melting point, poured into a container, and then air cooled under controlled conditions. The sampe is then conditioned at test temperature in a water bath. Penetration is measured with a penetrometer, which applies a standard needle to the sample for 5 seconds under a load of 100 grams.

A second characteristic of the most desired hot melt suspending media is a melting point of from 60°C to 140°C. A more preferred melting point for the waxes or resins is from 70°C to 100°C. Also relative to the melting point, the coating composition should set rapidly after application to the particular substrate for good results. More particularly, a melting range limitation, or in other words range of temperature in which the liquid hot melt composition sets into a solid composition, which we have found practical is from 1°C to 15°C. The preferred setting time is from 0.5 seconds to 5 seconds while the most preferred setting time is from 0.5 seconds to 2 seconds. While melting ranges of more than 15°C can be used the time necessary for such a coating composition to set requires special apparatus and handling and makes use of these hot melt compounds less commercially attractive.

The hot melt waxes and resins should also have a low viscosity when in a molten state in order to best facilitate ease of spreading on the substrate. For best results we have found that the hot melt suspending media should suitably have a viscosity of less than 120 centiposes at a temperature of approximately 5° above the melting point of the particular hot melt suspending medium. In addition, it is preferred that the hot melt wax or hot melt suspending media have a light colour in order to be compatible with the final paper or plastic product being produced. This means that it is preferred for the hot melt to be white or transparent after application to the particular substrate being coated.

The preferred waxes, resins and other hot melt suspending media preferably are polar. By polar it is meant that a certain amount of polarity is characteristic of the preferred waxes, the polar compositions being characterized by the presence of functional groups selected from carboxyl, carbonyl, hydroxyl, ester, amide, amine, heterocyclic groups, and combinations thereof. An alternative but less preferred arrangement involves the use of non-polar hydrocarbon waxes which should be used in conjunction with a dispersing agent.

The additives which may be included in the hot melt CB coating composition are typically an opacifying agent such as titanium dioxide or clay, a stilting agent such as Arrowroot starch and wax modifying agents such as polyvinyl acetate, isophthalic polyester, or any other resin materials soluble or dispersible in the main wax and which improves wax quality.

The method of dispersing the microcapsules in the hot melt suspending media is also of some importance since, likewise, a process which prevents significant agglomeration of the microcapsules should be used for good results. In the preferred process the microcapsules are formed into an aqueous slurry containing approximately 40% solids and are then spray dried to form a free-flowing powder. The free-flowing microcapsules are stirred into a molten phase of a suspension medium, such as a wax, a mixture of waxes, a resin or mixture thereof to form a smooth dispersion of microcapsules in the continuous molten phase. This hot melt can then be coated or printed, by gravure, blade coating, flexography or other means on to the continuous web. The hot melt system sets substantially immediately after application to the web and forms an excellent marking sheet.

In the most preferred arrangement a dispersing agent is added to the microcapsules prior to combining the microcapsules with the hot melt suspending medium. A preferred group of dispersing agents are the anionic dispersing agents, many of which are commercially available. A preferred group of anionic dispersing agents includes the sodium salts of condensed naphthalene sulphonic acids, the sodium salts of polymeric carboxylic acids, the free acids of complex organic phosphate esters, sulphated castor oil, poly-(methyl vinyl ether/maleic anhydride) and combinations thereof. The most preferred dispersing agent is sulphated castor oil. The dispersing agent is suitably added to the microcapsules in an amount of from 0.1% to 10% based on the dry weight of the microcapsules. A preferred range of addition is from 0.5% to 5% based on the dry weight of the microcapsules while a most preferred range is from 1% to 3% based on the dry weight of the microcapsules.

In the most preferred arrangement a dispersing agent is added to the microcapsules prior to combining the microcapsules with the hot melt suspending medium. In some instances the dispersing agent and the wall forming material are one and the same and the wall forming material not actually used in the microcapsule wall formation is present in hot melt coating dispersion as a dispersing agent. Although as described above many of the well-known, commercially available dispersing agents can be used in the process secondary dispersing agents that may be present as excess wall forming material include: hydroxypropylcellulose, gum arabic, gelatin, polyvinyl alcohol, carboxymethylcellulose, and mixtures of the above.

While the dispersing agent can be added at any point in the process prior to the setting of the coating composition, to achieve the most desirable results the dispersing agent should be added to the microcapsules prior to combining the microcapsules with the hot melt suspending medium. The particular amount of dispersing agent used is dependent on several variables including the particular type of microcapsule used, the particular type of hot melt suspending medium, the concentration of the aqueous microcapsular slurry, the viscosity of the hot melt suspending medium and the desired final coated product. We have found an addition based on the weight of the microcapsules of from 0.1 part by weight to 10 parts by weight to represent a practical range. A preferred range of addition would be from 0.5 to 5 parts by weight while the most preferred range of addition would be from 1 to 3 parts by weight.

The chromogenic coating composition can be applied to a substrate, such as paper or a plastics film by any of the common paper coating processes as developed above such as roll, blade coating or by any of the common printing processes, such as gravure, or flexographic printing. The rheological properties, particularly the viscosity of the coating composition, can be adjusted for each type of application by proper selection of the type and relative amounts of hot melt suspending media. While the actual amount of the hot melt coating dispersion applied to the substrate can vary depending on the particular final product desired for purposes of coating paper substrates CB coat weight of from 1 pound to 8 pounds per 3300 square feet of substrate have been found by us to be practical. The preferred range of CB coat weight application is from 2.5 pounds to 5 pounds per 3300 square feet of substrate, while the most preferred range is from 3 pounds to 4 pounds per 3300 square feet of substrate. If the CB chromogenic materials and a colour developer (CF) are combined into a single or self-contained chromogenic coating composition practical coat weights include from 2 pounds to 9 pounds per 3300 square feet of substrate, the preferred coat weight is from 3 pounds to 6 pounds per 3300 square feet, and the most preferred range is from 4 pounds to 5 pounds per 3300 square feet of substrate.

These hot melt coating dispersions or hot melt coating compositions can be set by any cooling means. Preferably a chill roll is used on the coating apparatus which cools the hot melt coating immediately after coating, but it is also quite common to simply allow the coating composition to cool naturally by atmospheric exposure. As the temperature of the coating composition is substantially higher than room temperature and in light of the fact that the coating thickness is generally less than 50 microns it can be seen that when spread out over a substrate the hot melt material cools very rapidly. The actual exposure or chill time necessary for setting of the chromogenic coating composition is dependent on a number of variables, such as coat weight, the particular hot melt suspending medium used, type of cooling means, temperature of cooling means and others.

The choice of wall-forming material and hot melt suspending media is important since certain microcapsules having walls of hydroxyethylcellulose when made by certain patented process and certain polyamides tend to agglomerate even in polar waxes. Agglomeration is undesirable since this prevents uniform distribution of the chromogenic material on the sheet. This may adversely affect transfer and uniformity of the intensity of the formed image.

The particular method of encapsulation or the particular encapsulated chromogenic material are not asserted *per se* to be the inventive feature so far as the present invention is concerned. Rather, there are described in the patent literature various capsular chromogenic materials which may be used. Such chromogens have been encapsulated in gelatin wall-forming materials (see U.S. Patents No. 2,730,456 and 2,800,457) including gum arabic, in polyvinyl alcohol, in carboxymethylcellulose, in resorcinol-formaldehyde wall-formers (see U.S. Patent No. 3,755,190), isocyanate wall-formers (see U.S. Patent No. 3,914,511) and hydroxypropylcellulose (see British Patent Specification No 1,468,130, in addition to mixtures of the above. Microencapsulation has been accomplished by a variety of known techniques including coacervation, interfacial polymerization, polymerization of one or more monomers in an oil, various melting, dispersing and cooling methods, and spray drying methods. Compounds which have been found preferable for use as wall forming compounds in the various microencapsulation techniques include: hydroxypropylcellulose, carboxymethylcellulose, gelatin, melamineformaldehyde, polyfunctional isocyanates and prepolymers thereof, polyfunctional acid chlorides, polyamines, polyols, epoxies and mixtures thereof.

Particularly well-suited to use in the practice of the present invention are microcapsules of a hydroxypropylcellulose (HPC) material. This is because such microcapsules are easily dispersed in most hot melt media. If necessary, a small amount of dispersing agent as described above can also be added to improve the dispersion. In addition, the HPC capsules have good permeability, strength, and temperature characteristics.

For additional description of hot melt systems which may be utilised in the practice of the present invention, the reader is referred to our co-pending British Patent Application 19423/77 (Serial No).

Our co-pending British Patent Application No 19424/77 (Serial No) includes a cross reference to the present application and is concerned with pressure-sensitive carbonless sheet sets involving the use of a meltable colour developer in production of a record sheet. The process described in the said specification is particularly useful for the production of manifold carbonless forms. Reference should be made to the text of the said specification for examples of non-aqueous solvent free coatings useful in the practice of the present invention.

RADIATION CURABLE SYSTEM

The second preferred coating method involves the use of radiation curable resins. As with the hot melt activation system the radiation curable resins can be used as either a CF or a CB coating but preferably are used as the CF coating system. The basic concept of the radiation curable activation system involves addition suitable chromogenic material such as a novolak resin to a liquid radiation curable material which can be solidified by exposure to radiation such as ultraviolet or electron beam. The liquid mixture containing the chromogenic material and the liquid radiation curable material is then applied as a thin film to the continuous web which is exposed to ultraviolet light to cure the coating.

The radiation curable chromogenic coating composition may consist of a dispersion of a chromogenic material in a liquid radiation curable substance. Examples of chromogenic materials which can be used in radiation curable systems in the practice of this invention can be found both among chromogenic materials which are soluble in the liquid radiation curable substance and among chromogenic materials which are insoluble in the liquid radiation curable substance. When the chromogenic materials are colour developers, they are preferably in microencapsulated or dispersed form. Insoluble chromogenic colour developers, for use in preparing carbonless record sheets, such as the acid clays, are suitably present in the coating composition as a dispersed particulate solid. Most organic colour developers are soluble in the radiation curable substance.

The coating composition may contain additional materials which function as photoinitiators. Addition of these materials depends upon the particular method of curing the chromogenic coating. Filler materials can also be added to modify the properties of the cured film. The use of non-reactive solvents, which require heat to remove them during the drying or curing of the coated film, is avoided.

The chromogenic colour developers we have found most useful in the radiation curable embodiment are the acidic electron-acceptors and include acid clays such as attapulgus clay, and silton clay, phenolic materials such as 2-ethylhexylgallate, 3,5-di-tert-butyl salicylic acid, phenolic resins of the novolak type and metal modified phenolic materials such as the zinc salt of 3,5-di-tert-butyl salicylic acid and the zinc modified novolak type resins. The most preferred chromogenic colour developers are the novolaks of p-phenylphenol, p-octylphenol and p-tert-butylphenol. Mixtures of these colour developers may be used, if desired. They may suitably be present in the liquid chromogenic composition in an amount of from 25% to 75% by weight of the chromogenic composition. The preferred range is from 35% to 65%, and the most preferred range is from 40% to 55%.

Radiation curable substances which we have found useful comprise the free radical polymerizable ethylenically unsaturated organic compounds. These compounds must contain at least one terminal ethylenic group per molecule. They are liquid and act as dispersing media for the chromogenic material and other ingredients of the coating composition. They are curable to a solid resin when exposed to ionizing or ultraviolet radiation. Curing is by polymerization.

A preferred group of radiation curable compounds are the polyfunctional ethylenically unsaturated organic compounds which have more than one (two or more) terminal ethylenic groups per molecule. Due to the polyfunctional nature of these compounds, they cure under the influence of radiation by polymerization, including crosslinking, to form a hard dry tack-free film.

Included in this preferred group of radiation curable compounds are the polyesters of ethylenically unsaturated acids such as acrylic acid and methacrylic acids, and a polyhydric alcohol. Examples of some of these polyfunctional compounds are the polyacrylates or methacrylates of trimethylolpropane, pentaerythritol, dipentaerythritol, ethylene glycol, triethylene glycol, propylene-glycol, glycerin, sorbitol, neopentylglycol and 1,6-hexanediol, hydroxy-terminated polyesters, hydroxy-terminated epoxy resins, and hydroxy-terminated polyurethanes and polyphenols such as bisphenol A. An example of a polyacrylate of a hydroxy-terminated polyurethane found to be useful is di(2′ ∂ acryloxyethyl)-4-methylphenylene diurethane.

Also included in this group are polyallyl and polyvinyl-compounds such as diallyl phthalate and tetrallyloxyethane, and divinyl adipate, butane divinyl ether and divinylbenzene. Mixtures of these polyfunctional compounds and their oligomers and prepolymers may be used if desired.

A second group of radiation curable compounds are the monofunctional ethylenically unsaturated organic compounds which have one terminal ethylenic group per molecule. Examples of such monofunctional compounds are the C_8 to C_{16} alcohol esters of acrylic and methacrylic acid, and styrene, substituted styrenes, vinyl acetate, vinyl ethers and allyl ethers and esters. In general, these compounds are liquid and have a lower viscosity than the polyfunctional compounds and thus may be used to reduce the viscosity of the coating composition to facilitate coating by any desired method. These compounds are radiation curable and react with the ethylenically unsaturated polyfunctional organic compounds during radiation curing to give a hard drying flexible film. Compounds having only one terminal ethylenic group may be used alone as the radiation curable substance. However, the resultant radiation cured film may be rather soft and pliable and may be somewhat too tacky for commercial use. The preferred radiation curable substance is a mixture containing one or more polyfunctional compounds and one or more monofunctional compounds. By proper selection of these compounds a chromogenic coating composition having the desired coating characteristics for any type of coating application can be made, and a hard, flexible tack-free radiation cured film can be obtained. In general, the most desired films are obtained by using a radiation curable substance comprising from 33% to 67% of the polyfunctional compounds to 33% to 67% of the monofunctional compounds.

A photoinitiator is preferably added to the coating compositions if the composition is to be cured by ultraviolet radiation. A wide variety of photoinitiators are available which serve well in the system described. The preferred photoinitiators are the benzoin alkyl ethers, such as, Vicure 30 (a mixture of alkylbenzoin ethers manufactured and sold by Stauffer Chemical Co., Westport, Connecticut), benzoin butyl ether (Vicure 10), Stauffer), benzoin methyl ether, and α,α-diethoxyacetophenone. Other photoinitiators which have been used are benzophenone,4,4′ -bis-(dimethylamino) benzophenone, ferrocene, xanthone, thioxanthane, α,α-azobisisobutylnitrile, decabromodiphenyl oxide, pentabromomon chlorocyclohexane, pentachlorobenzene, polychlorinated biphenyls such as the Arochlor 1200 series (manufactured and sold by Monsanto Chemical Co., St Louis, Missouri - Arochlor is a Registered Trade Mark) benzoin ethyl ether, 2-ethyl-anthroquinone, 1-(chloroethyl)naphthalene, decyl chloride, chlorendic anhydride, naphthalene sulfonyl chloride and 2-bromoethyl ethyl ether Zinc oxide combined with a small quantity of water also serves as a good substitute photoinitiation system. The amount of photoinitiator added can suitably be from 0.2% to 10% by weight of the coating composition, with a preferred range being from 3% to 8% by weight.

Photoinitiation synergists may also be added to the ultraviolet curing coating compositions. Photoinitiation synergists serve to enhance the initiation efficiency of the photoinitiators. The preferred synergists are chain transfer agents, such as the tertiary alcoholamines and substituted morpholines, such as triethanolamine, N-methyldiethanolamine, N,N-dimethylethanolamine and N-methyl-morpholine. The amount of photoinitiation synergist added can suitably be from 0.2% to 10% by weight of the coating composition, with a preferred range being from 3% to 8% by weight.

Filler materials may be added as flattening agents, particularly to colour developing coating compositions, to reduce the glossy appearance of the cured resin films and preserve the appearance of the substrate prior to coating. Thus a bond paper which has been coated with the coating composition and which is then cured to a solid film gives the impression of being an uncoated bond paper.

The preferred filler materials are of the colloidally precipitated or fumed silicas. Typical of the silicas which can be used are the ones tradenamed LoVel 27 (a precipitated silica manufactured and sold by PPG Industries, Inc., Pittsburgh, Pennsylvania) Syloid 72 (a hydrogel silica manufactured and sold by W. R. Grace & Co., Davison Chemical Division, Baltimore, Maryland) and Cab-o-sil (Registered Trade Mark) (a fumed silica manufactured and sold by Cabot Corporation, Boston, Massachusetts). All of these silicas are known to give an initial bluish colour with colour precursors such as crystal violet lactone. However, this colour fades quickly on aging. Using the record sheet so produced, the developed colour does not fade easily. It is theorized that the filler material through its large surface area provides for increased porosity of the cured resin film, thereby promoting more rapid and more complete transfer of an oily solution of colour precursors from a transfer sheet to the record sheet surface. The amount of filler materials can suitably be up to 15% by weight of the coating composition and the preferred range is from 10% to 15% by weight.

Mixing of the ingredients of the coating composition is not critical. Ingredients can be added one at a time or they can be added all at once and stirred until they are uniformly mixed. We have obtained good results when the ingredients making up the radiation curable substance and the chromogenic material are heated with stirring to facilitate blending of these ingredients. If used, the photoinitiator, photoinitiation synergist and filler are best added when the coating composition is at or slightly above room temperature. It is also preferable to add microcapsules at room temperature.

The chromogenic coating compositions can be applied to a substrate, such as paper or a plastics film by any of the common paper coating processes such as roll, air knife, or blade coating, or by any of the common printing processes, such as offset, gravure, or flexographic printing. The rheological properties, particularly the viscosity, of the coating composition, can be adjusted for each type of application by proper selection of the type and relative amounts of liquid radiation curable compounds. While the actual amount of chromogenic coating composition applied to the substrate can vary depending on the particular final product desired, for purposes of coating paper substrates we have found that for the CF chromogenic coating compositions from 0.2 pounds to 8 pounds per 3300 square feet of substrate represents a practical range of coat weights, the preferred range being from 0.5 pounds to 4 pounds per 3300 square feet of substrate and the most preferred range from 1 pound to 3 pounds per 3300 square feet of substrate. If the CF and CB chromogenic materials are combined into a single or self-contained chromogenic coating compositions practical coat weights we have found to include from 2 to 9 pounds per 3300 square feet of substrate. The preferred coat weight is from 3 pounds to 6 pounds per 3300 square feet, and the most preferred range is from 4 pounds to 5 pounds per 3300 square feet of substrate.

These coating compositions can be cured by any free radical initiated chain propagated addition polymerization reaction of the terminal ethylenic groups of the radiation curable compounds. These free radicals can be produced by several different chemical processes including the thermal or ultraviolet induced degradation of a molecular species and any form of ionizing radiation utilizing alpha-particles, beta-rays (high-energy electrons), gamma-rays, x-rays and neutrons. The actual exposure time necessary for curing of the chromogenic coating composition is dependent on a number of variables such as coat weight, coat thickness, the particular radiation curable substance, type of radiation, source of radiation, radiation intensity and distance between the radiation source and the coated substrate. In most instances curing is virtually instantaneous with actual curing times ranging from 1 millisecond to 2 seconds. The preferred curing time is from 0.1 second to 1 second, while the most preferred curing time is from about 0.3 second to about 0.6 second.

The preferred curing process is by exposure of the coating composition to ultraviolet radiation having a wavelength of 2000°A to 4000°A. For ultraviolet curing to occur the composition must contain suitable ultraviolet absorbing photoinitiators which will produce polymerization initiating free radicals upon exposure to the radiation source. A typical ultraviolet source suitable for this type of curing process is a Hanovia (Registered Trade Mark) 200 watt medium pressure mercury lamp. Curing efficiencies of the coating composition are dependent on such parameters as the nature of the radiation curable substance, atmosphere in contact with the coating, quantum efficiency of the radiation absorbed, thickness of coating and inhibitory effects of the various materials in the composition.

In the ionizing radiation induced curing of these coating compositions a specific radiation absorbing material (photoinitiator) is not necessary. Exposure of the coating composition to a source of high energy electrons results in the spontaneous curing of the composition to a hard, tack-free coating. Any of a number of commercially available high energy electron beam or linear cathode type high energy electron sources are suitable for curing these compositions. Parameters such as the atmospheric environment and inhibitory effects of the various materials in the composition play an important role in the determination of the curing efficiency of these compositions.

For additional description of radiation curable systems which may be utilised in the practice of the present invention, the reader is referred to our copending British Patent Application 19420/77.

A particular advantage of this coating process is that it permits the use of spot coating. Spot coating refers to the fact that less than 100% of the surface area of the individual sheet whether it is a CF, CB, self-contained or other sheet need be coated. For instance, the area of the paper normally associated with the margin on either side of the printed side portion need not be coated. This, of course, represents a significant cost advantage in the saving of encapsulated material. The encapsulated material is one of the most costly materials which goes into the forms manufacture. Therefore by eliminating certain sections of the web surface that need to be coated a significant cost saving can be appreciated. The use of spot printing can vary from simply omitting coating of the margin portion of the paper to the making of a form wherein only a single line is actually coated. At the same time, forms such as computer printouts can be made wherein only every other line is coated. Thus it can be seen that from 10% to 95% of the surface area of the paper need not be coated. In most instances it would be most convenient to simply not print the marginal areas of the paper which would save from 10% to 30% of the total encapsulated material cost.

Upon completion of the coating operation and the appropriate setting or curing operation the web or substrate is wound on to a mandrel and placed in storage. The individual roll is held in storage and then combined with a predetermined number of additional coated or uncoated webs during the collating operation. The term collating refers to a step in the process whereby a plurality of individual coated or uncoated webs are arranged in appropriate order, as, for example, CB coating next to a CF coating. The term collating means shall be understood to refer to apparatus or other means for accomplishing the desired arrangement of the plurality of individual webs.

An adhesive step is completed prior to, during or after the collating operation. The adhesive material is applied or the adhesive means are used generally only after a plurality of the individual webs have been removed from storage and are being processed, i.e. collated. The adhesive is applied to one or more edges of the plurality of individual webs or in the alternative an adhesive can be applied over all or a portion of the surface of one or more of the individual webs. Any of the well known glues or adhesives normally used in the paper industry are usable in the adhesion means. Alternative adhesion methods include bonding members such as adhesive strips, staples, V-shaped slits and other less commonly encountered methods. While the adhesion step has been described as generally occurring after the coating step or steps and before the collating and finishing steps it can be completed at any convenient point during the process. More particularly, in the most preferred embodiment of the process a liquid adhesive is applied by adhesion means prior to the collating step and the individual webs are combined during the finishing step. Thus in the most preferred embodiment an adhesive is applied prior to collating but the webs themselves are not actually placed in combination with one another until the finishing step. In another embodiment the adhesion means may be omitted altogether and the individual webs are not necessarily joined to one another but may be merely arranged in the appropriate sequence with one another. In still another embodiment the adhesion means may be located after the collating means in the operating sequence. In a further embodiment the collated and finished sheets may be bound or adhered to one another after the finishing step. The particular sequence and apparatus used in the adhesion means, collating means and finishing means is a matter of individual choice and is dependent upon the final product desired. No special significance is attached to the particular order or occurrence of these steps.

After, during or prior to the adhesive operation the continuous substrates are advanced to collating means. The collating means arrange the various individual webs into the proper relationship with one another. This can involve the arrangement of colours, as for example if the customer copy or if the original is white the customer copy is green and the file copy is red, or in the alternative this can involve the arrangement of particular sheets so that the CB and CF coated sheets will be in contact when the final form is made. If self-contained type carbonless paper is used the coated surface of the paper is the topmost surface of each sheet. All of this is done by prearranged programming of the collating apparatus.

After collating the forms are fnished by any of a variety of steps. The finishing operation may suitably involve the steps of attaching the sheets to one another, partitioning the sheets into suitable sizes, stacking the sheets into appropriate stacks and/or packaging the sheets in addition to other steps which may be desired.

WHAT WE CLAIM IS:-

1. A process for the production of a manifold carbonless form, comprising: providing a plurality of continuous webs; advancing each web of said plurality of continuous webs at substantially the same speed, said plurality of continuous webs being spaced apart and being advanced in a cooperating relationship with one another; marking at least one web of said plurality of continuous webs with a pattern; applying at least one non-aqueous, solvent-free coating of chromogenic material (as herein defined) to at least a portion of at least one web of said plurality of continuous webs; setting said coating; collating said plurality of continuous webs; and placing said collated continuous webs in contiguous relationship to one another to create a manifold form.

2. A process for the production of a manifold carbonless form, comprising: providing a continuous web; marking at least one surface of said continuous web with a pattern; applying at least one non-aqueous, solvent-free coating of chromogenic material (as hereindefined) to at least a portion of at least one surface of said continuous web; setting said coating to form a marked, coated continuous web; combining said marked, coated continuous web with at least one additional continuous web to form a plurality of

continuous webs, each of said additional continuous webs having at least a portion of at least one surface thereof coated with at least one non-aqueous, solvent-free coating of chromogenic material (as hereindefined), said coatings being set; collating said plurality of coated continuous webs; and placing said collated continuous webs in contiguous relationship to one another to create a manifold carbonless form.

3. A process according to Claim 1 or Claim 2, further comprising the step of finishing said collated, contiguous webs.

4. A process according to Claim 3, wherein said finishing step includes: fixably combining said plurality of collated, contiguous webs into a single manifold substrate; partitioning said single manifold substrate into a plurality of sheets, each sheet of said plurality of sheets being of a size appropriate for use as a manifold carbonless form; stacking said sheets; and packaging said stacked sheets.

5. A process according to any preceding claim, wherein said continuous webs are of paper.

6. A process according to any preceding claim, wherein said plurality of continuous webs comprise from 2 to 6 continuous webs.

7. A process according to any preceding claim, wherein said marking is by means of printing.

8. A process according to Claim 7, wherein said marking is by offset printing means.

9. A process according to any preceding claim, wherein said application or at least one of said applications of a non-aqueous, solvent-free coating is by means of printing.

10. A process according to any preceding claim, wherein said or at least one of said non-aqueous, solvent-free coatings includes a hot melt suspending medium.

11. A process according to Claim 10, wherein said hot melt suspending medium comprises a low molecular weight polar wax.

12. A process according to Claim 10 or Claim 11, wherein said setting is by means of temperature decrease resulting from atmospheric exposure.

13. A process according to any one of Claims 1 to 9, wherein said or at least one of said non-aqueous, solvent-free coatings includes a radiation curable material.

14. A process according to Claim 13, wherein said radiation curable material comprises a mixture of ethylenically unsaturated organic compounds, a portion of said compounds having one terminal ethylenic group per molecule and another portion of said compounds having more than one terminal ethylenic group per molecule.

15. A process according to Claim 13 or Claim 14, wherein said setting is by means of exposure to radiation.

16. A process according to Claim 15, wherein said radiation is ultraviolet radiation.

17. A process according to Claim 15, wherein said radiation is electron beam radiation.

18. A process according to any preceding claim, wherein said coating composition is applied to from 30% to 70% of the surface area of at least one continuous web of said plurality of continuous webs.

19. A process according to any preceding claim, wherein said chromogenic material is capsular.

20. A process according to any preceding claim, wherein a first said non-aqueous, solvent-free coating is applied to the back surface of at least one continuous web of said plurality of continuous webs; and a second said non-aqueous, solvent-free coating is applied to the front surface at least one web of said plurality of webs, said second coating being reactive with said first coating to form a colour.

21. A process according to anyone of Claims 1 to 18, wherein the front surface of each of said webs is marked; wherein a first said non-aqueous, solvent-free coating, in which the chromogenic material includes a colour precursor of the electron donating type, is applied to at least a portion of the back surfaces of all except one of said plurality of webs; a second said non-aqueous solvent-free coating, in which the chromogenic material includes a colour developer of the electron accepting type, is applied to at least a portion of the front surfaces of all except one web of said plurality of webs; the colour developer being reactive with said colour precursor to form an image, and at least one of said colour precursor and said colour developer being encapsulated; and wherein said collating is performed such that the front surface of the resultant topmost web in said manifold is marked but does not have any non-aqueous, solvent-free coating, such that the back surface of the resultant bottom-most web of said manifold is neither marked nor coated with a non-aqueous solvent-free coating, and such that all the remaining front and back surfaces of said plurality of webs are coated.

22. A process for the production of a manifold carbonless form, substantially as hereinbefore described.

23. A manifold carbonless form whenever produced by a process according to any preceding claim.

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