Oct. 8, 1957 D. A. NEWMAN ET AL 2,808,778

PLANOGRAPHIC PRINTING PLATE

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Fig. 1

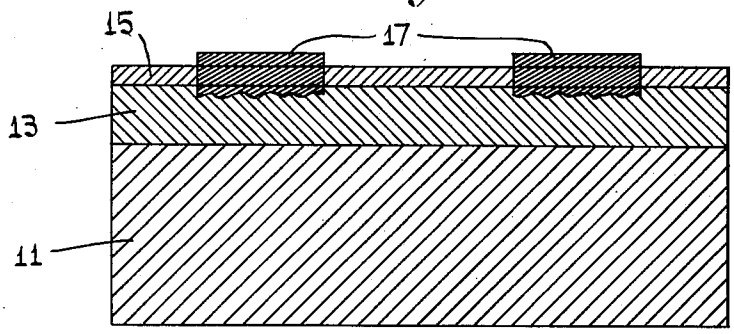
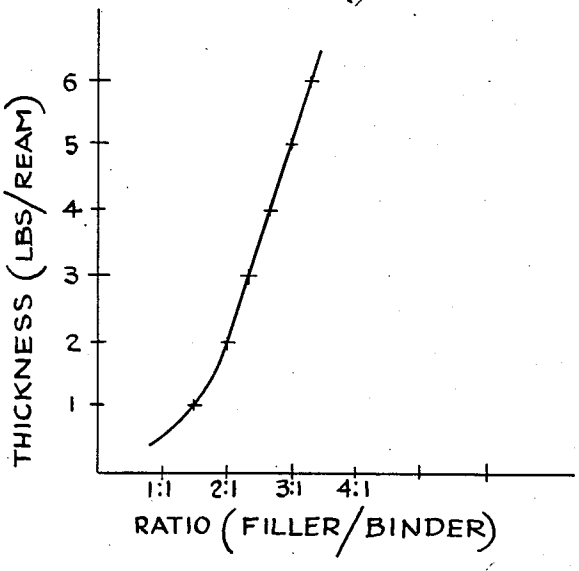


Fig. 2



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PLANOGRAPHIC PRINTING PLATE

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Application September 16, 1953, Serial No. 380,446

6 Claims. (Cl. 101—149.2)

This invention relates to the manufacture of planographic printing plates, suitable for use in planographic printing processes in which the surface of a plate on which an image is formed of ink-receptive material (e. g., a waxy or greasy ink) is wetted with an aqueous ink-repelling fountain fluid, then inked over to deposit ink only on the image, the latter being then transferred to a sheet of paper, usually by way of a blanket as in offset printing, the image being repeatedly reinked and the foundation being maintained wet and hence ink-repellent as repeated copies are printed.

In the following specification and claims where it is found necessary to refer to coating thicknesses the same are expressed in terms of pounds per ream, and will be understood to refer to a ream of 500 sheets, 25" x 38".

More specifically this invention relates to planographic printing sheets or plates having a paper foundation in which the printing surface is in the form of a film applied to the paper foundation and in which the surface film has greater flexibility and homogeneity and less curling tendency than that of prior sheets, and in which the sheet lends itself to the improved retention of certain types of planographic images presently regarded as somewhat difficult of attachment to coated paper printing surfaces, as well as to improved surface retention of the ink-repellent moisture.

The invention, in certain of its aspects, relates to the manufacture of plates in which the printing surface layer comprises essentially carboxymethyl cellulose compounds and a filler of china clay or the like similar to the plates disclosed in the prior application of Douglas A. Newman, Serial No. 637,088, filed December 22, 1945, now Patent No. 2,655,864. In said application is disclosed the method of making a plate, and the plate itself, in which the printing surface or coating is of an initially soluble carboxymethyl cellulose compound which is dried and rendered insoluble by an aftertreatment with an aqueous solution including a copper salt, an iron salt, an aluminum salt, or a chromium compound, or mixtures of a copper salt with certain of the others. This procedure has resulted in the production of commercially acceptable printing plates which include a surface of a carboxymethyl cellulose compound. While the plates and the prints produced thereby were of good commercial quality, certain problems relating to their manufacture and use were experienced which it is the object of this invention to overcome.

The method of insolubilization of the printing surface coating employed in constructing plates according to the teachings of said application rendered it important to include in the surface coating a ratio of clay or other suitable filler to the carboxymethyl cellulose binder of about 4:1, or preferably greater. These ratios were found preferable in order that the coating might have a sufficient degree of openness to take up the insolubilizing solution and distribute it as nearly as possible to all parts of the carboxymethyl cellulose in the surface layer. Ac-

cording to the present invention it is possible to insolubilize the coating throughout without regard to its openness so that the ratio of filler may be varied at will to give ratios best suited to other considerations.

The product of this method of insolubilization, i. e., the method of coagulation of a carboxymethyl cellulose product with mixtures of a copper salt with an iron, aluminum or chromium compound, or mixtures of a copper salt with compounds of two or all of said metals has been determined as the most successful form of carboxymethyl cellulose deposit known to date insofar as the formation of planographic printing surface is concerned. Up until the present invention was made, however, it was necessary to carry on this insolubilization primarily as an aftertreatment applied to the dried soluble layer. The placing of a self-insolubilizing layer of carboxymethyl cellulose including a copper salt was disclosed and claimed in the application of Douglas A. Newman, Serial No. 318,340, filed November 1, 1952, but that application disclosed specifically a solution which was slightly alkaline in pH to maintain the copper salts in solution, and which would throw down the known suitable coagulant iron and aluminum compounds, if present, as precipitates without giving a chance for their reaction with the carboxymethyl cellulose.

The present invention has for its object the preparation of a planographic plate from a coating solution of carboxymethyl cellulose which is self-insolubilizing on drying and which, at the same time, includes reagents of such character that the resulting layer will still be made up of the copper derivative of carboxymethyl cellulose mixed with the iron, aluminum or chromium derivatives or mixtures thereof in the desired proportions.

Inasmuch as the cost of making planographic plates depends largely upon the number of treating steps to which they must be subjected, it is another object of the present invention to provide a paper planographic printing plate in which the surface coating is of metal substituted compounds of carboxymethyl cellulose of the appropriate mixture for producing printed copies of the highest quality, but a coating which is still of such a nature that it can be applied in a single coating operation rendering a film which automatically becomes water insoluble upon drying so that a single coating treatment is involved in applying the insoluble surface layer.

It is a feature of this invention that carboxymethyl cellulose coatings of self-insolubilizing nature made to conform to the viscosities, surface tensions and filler percentages found in the disclosure of said Newman application, Serial No. 318,340, for the purpose of providing a treatment for pre-imaged sheets to convert them into copy-producing masters, can be made to include the preferred aluminum ferric and chromium insolubilization factors in proper proportion, in addition to the copper ions therein disclosed.

It has been discovered that planographic surface coatings as heretofore constructed, in some instances, are subject in some degree to difficulties such as cracking, during flexure, shattering under a type blow, flaking, picking and the like. Another difficulty which is sometimes experienced is that of excessive absorptivity of the printing layer and underlying layers so that moistening fluids tend to drain rapidly away from the surface in the background areas and leave the same dry after any slight interruption in printing. All of these difficulties, it has been discovered, stem primarily from the percentage of filler which the coating must carry, and the thickness of the coating. However, as previously pointed out, a certain percentage of filler has been heretofore required in printing surfaces of carboxymethyl cellulose to insure proper insolubilization by the most desirable treatments

known from the standpoint of producing good planographic properties. However, without particular regard to the nature of the insolubilization treatment required by the binding ingredient, it is also known that with planographic layers as heretofore commonly used, certain filler percentages were essential in order to provide proper acceptance of certain types of images, especially those produced by carbon paper, and that drastic reduction in filler percentages, even if otherwise permissible, were not allowable because the power of the surface to accept and retain such images would be adversely affected beyond the point of commercial acceptability.

Similarly, attempts to cause the printing layer to be made thinner than ordinarily deposited (e. g., in the neighborhood of 8 pounds minimum per ream) principally for reasons of economy, resulted in failure because the coatings with usual paper-making equipment and procedures could not be sufficiently uniformly deposited to cover all parts of a sheet equally. In many cases the areas of show-through of the oleophilic foundation or undercoating were sufficient to cause inacceptable specks and background tone on the printed copies and would be so frequent as to prevent plates thus coated from being commercially accepted.

It has bene discovered, however, in connection with the present invention, that insofar as acceptance of images is concerned, the filler ratio is not the only governing factor, and that filler percentages can be reduced provided that the thickness of the layer is also simultaneously reduced, and that under these circumstances acceptance for difficultly received images (e. g., those formed using carbon paper) can be held up to standard and may, in fact, even be improved.

The investigations leading up to the present invention have also resulted in the discovery that procedures and equipment are available for uniformly applying to paper water-dispersed coatings which are much thinner than those previously regarded as having the minimum practical thickness for printing plates and for so applying the coatings that gaps and thin spots, if they occur at all, do not appear with injurious frequency. While the procedures which make it possible to apply these thin coatings with accuracy and uniformity will usually involve equipment conversion, which would ordinarily be avoided if possible, it has been demonstrated that a number of unexpected and important advantageous effects result directly from the provision of thinner coatings which make it, in fact, economically feasible if not preferable to make the effort to convert to the new procedures and equipment when necessary to their production.

Another point in connection with coating thickness is the consideration that thin coatings of fairly uniform thickness necessarily depend to a large extent for their uniform quality on the smoothness and low porosity or permeability of the undercoating or surface which receives them. Heretofore it has been an important consideration in plate manufacture that any undercoating present should bond firmly with the printing surface coat regardless of any considerations of smoothness of the undercoat, and within limits the degree of bond was generally considered as somewhat improved as smoothness decreased and porosity or permeability of the undercoat increased. According to the present invention it has been discovered that the importance of the degree of bond diminishes at least as rapidly as the thickness of the coating is reduced, so that even with the smooth, relatively impermeable surfaces necessary to the casting of a thin surface film of uniform thickness, the bonding tendencies are not only sufficient to maintain equivalent excellence of operation, but the performance of the sheet can in fact be improved by thinning the surface coating in spite of what would ordinarily be considered degrading changes in the character of the undercoat necessary to this end.

It is another object of the present invention, therefore to provide a planographic printing surface coating on a paper planographic plate which has a thickness corresponding to a coating weight of less than 6 pounds per ream, and in the preferred case less than 4 pounds per ream.

One of the important advantages of the thin surface coatings of the present invention is that the image, instead of being impressed on and attaching itself to the surface coating of the plate, may be so placed that it appears to penetrate and probably does penetrate the coating and becomes firmly attached to an underlying oleophilic layer—its degree of attachment to the plate thus being controlled primarily by the characteristics of the underlying layer without placing particular reliance on the characteristics of the surface layer. To this end it is still another object of the invention to provide a planographic printing plate having an image-receptive, moisture-resistant undercoating, and a thin surface coating including a hydrophilic binder of a thickness corresponding to a coating weight of less than 6 pounds per ream and in the preferred case less than 4 pounds per ream.

Additional features and advantages will hereinafter appear.

In the accompanying drawing:

Figure 1 is an enlarged schematic section of a planographic plate bearing an image, and made according to the present invention.

Fig. 2 is a chart illustrating the effect of coating thickness on minimum permissible filler ratios.

In carrying out the present invention we provide a foundation such as a sheet or web **11** of paper. The paper **11** may be treated in a known fashion with suitable impregnating compositions to give it good wet strength and wet extensibility if a plate which is to provide long printing runs is being made. On the other hand, if a plate for very short runs is required, it may sometimes be feasible to omit these treatments and use the paper without such impregnation as a foundation. Likewise a waterproofing undercoat **13** may be and is preferably applied to one side of the sheet, depending somewhat upon the degree of waterproofness required by the length of printing run expected. In most cases the waterproofing undercoat, if used, will be about 10 pounds per ream and may include such ingredients as hardened casein, a latex, or any film capable of forming a relatively waterproof barrier, attaching itself to the sheet and to the printing surface coating, and having substantial oleophilic properties. It will be understood, of course, that the cellulosic foundation sheet itself, impregnated or unimpregnated, and even when uncoated, is also normally preferentially oleophilic.

To the surface of the sheet or web provided with undercoat **13**, is applied a planographic printing coating **15** having a binder portion which consists of a water-soluble colloid which forms a water-insoluble film, or a film which is capable of being rendered water-insoluble after casting. The properties of the coating **15** must either be such that it has a hydrophilic-oleophilic balance suited to the reception of image material and ink when dry, the retention of such image material when subsequently wetted, and the reception and retention of moisture in the non-image areas; or such that it is slightly more hydrophilic than oleophilic.

In one aspect of the present invention various materials are usable as binders for this purpose, for example, casein admixed with small proportions of an aldehyde, carboxymethyl cellulose compounds, gum arabic in association with a chromate ion, and polyvinyl alcohol with a small proportion of a chromate. However, these are not to be considered as limiting, for almost without exception any composition based on a hydrophilic colloid found suitable for coating paper planographic plates, and which has properties permitting its placement in very thin but continuous coatings, can be employed in the present invention.

The discovery which is the core of the present inven-

tion is primarily the placing of the planographic surface coating in a continuous but extremely thin layer, a layer so thin in fact as to have been considered impractical heretofore. The thickness of this layer may be in the range of ½ pound to 6 pounds per ream with the most successful operation found in the range of ½ pound to 4 pounds per ream. Heretofore a minimum of 8 pounds per ream has been considered by the art as the practical lower limit for printing surface coatings of this nature because ordinary paper making procedures and equipment would not cast a coating sufficiently thin, which was also continuous and free from background specks in printing. Furthermore, to provide for a better and more continuous coating of any weight substantially less than 8 pounds per ream would entail the conversion of procedures and equipment adding significantly to the inconvenience and to some extent the cost of manufacturing the plates without any prospect for overcoming the difficulties normally entailed in reduction of coating thickness.

We have found that by taking the additional procedural steps necessary, e. g., extra calendering of the foundation web, or the undercoated foundation to reduce fiber eruption at the surface, and the use of special coating procedure and/or equipment, the placing of a thin but continuous coating of the planographic surfacing material is feasible in many cases and gives printing results entirely out of proportions to anything which could be expected by a mere reduction of the coating thickness. In fact normally any substantial reduction of the surface coating thickness would have been considered as a degradation of the plate quality. We have discovered on the contrary, that important improvements in the quality of the plate itself and the printing produced can be effected by this expedient.

The exact reason for the disproportionate success of the present lightweight coating as a printing layer is not entirely understood at present. It appears definitely, however, that both the tendency of the sheet to curl and the tendency of the coating to crack, or pick (separate from the foundation during printing), are reduced very sharply as the thickness of the coating is decreased and much more rapidly than any proportionate estimate would indicate. This effect takes place so markedly, in fact, that a sheet having a coating composition which causes inacceptable curl, cracking or picking at a thickness of 8 pounds per ream, is transformed to an acceptable sheet by the mere reduction of the coating layer thickness to below 6 pounds per ream without other change, and the possibilities in connection with most known coating formulations are reduced to a substantial certainty of successful operation at any coating thickness below 4 pounds per ream.

Another aspect in which the improved plates of the invention present superior printing results is in the matter of image life. The preparation of coating formulation so as to receive and tenaciously retain the oleous or other image forming material (while still being hydrophilic enough for background purposes) has been heretofore a matter of continuous concern in plate-making. It has been found that compositions which have been of borderline character or even inacceptable from the standpoint of image retention in prior ordinary use, but which are not actually repellent to the image material, perform with distinct acceptability when applied according to the principles of this invention. This is thought to be due to the possibility provided for the material of the image, such as image **17**, Fig. 1, to penetrate the surface printing layer and attach itself to the preferentially oleophilic surface of the web or waterproof substratum **13**, if present, and thus form a permanent image substantially free of any tendency to sharpen or fail during the printing run. This presumed arrangement is illustrated in the drawing by showing image portions **17** as extending deeper than the coating 15 and partially into layer **13**. It is not yet known whether the improved image connection is brought about by the mechanical force used in applying it, e. g., by a type impression or blow, or whether the oleous material of the image merely permeates the coating **15** as by capillary action, or both, but in any case it is readily demonstrable that the reduced coating thickness characteristic of this invention is the change which causes the observed image improvement.

Ancillary to the foregoing discovery of coating thickness was our additional discovery that filler percentages could be changed as the coating thickness was reduced. It has been known that inert absorbent fillers can be added to coating compositions for improving some of their printing properties. One of the most commonly used materials for this purpose is china clay. Such fillers are usually present in coatings in the proportion of between four and seven parts of filler to one part of binder (dry basis) in order to provide a surface which will readily accept and retain images placed by a type blow from a typewriter using a carbon paper imaging element. These proportions, however, tend to introduce other problems into the coating which must be otherwise overcome such as decreasing the tendency of the coating to bond to its foundation, and increasing the tendency of the coating to crack, emboss, or pick up on writing instruments. We have discovered not only that reducing the thickness of the coating reverses all of these tendencies in and of itself, but also that the coating composition can be prepared using a smaller proportion of clay without affecting its ability to accept and retain images formed by typing with carbon paper. According to the invention it has been determined that the minimum filler-binder ratios by weight suitable for carbon paper inscription are variable and are not directly proportional to the coating weights employed but are given with sufficient accuracy for practical purposes by the following table.

TABLE A

Coating Thickness (T) (pounds per ream)	Approximate Minimum Ratio of Absorbent Filler to Binder for Holding Carbon Images (R min.)
6	3.3:1
5	3:1
4	2.6:1
3	2.3:1
2	2:1
1	1.5:1
½	1:1

The values in the above table lie on a curve which is graphically represented in Fig. 2 of the drawing.

The reduction of the filler ratio from the usual values cooperates in an important manner with the reduced coating thickness by allowing the film of binder material to be more continuous and tougher so that, even though essentially thinner than coatings ordinarily employed, it will still resist the abrasion incident upon erasures and thus permit corrections. Likewise the reduced coating thickness assists the operation of the coating in accepting and holding the image as explained above so that the filler ratio can be significantly reduced when desired without also reducing the holding power of the printing surface for carbon paper images to less than acceptable values.

It has further been discovered that the lower filler content permitted by the coatings of lesser thickness as shown in Table A and Fig. 2 give outstandingly good results from the standpoint of moisture retention. Coatings having the filler ratios heretofore commonly used would invariably require special moistening for proper starting whenever a run was beginning or remoistening whenever a slight delay in printing occurred. It has been found, however, that when the ratio of filler to binder is 2:1 or less this is not the case. The moisten-

ing received by the plate in normal treatment by any average setting of the printing machine is sufficient to start the proper printing action of the plate almost at once, and also to provide immediate resumption of proper printing after any delay. This is of special importance in the case of systems plates where a few copies only are required, where set-up and starting time is a significant proportion of press operation time, and where long periods of time for adjusting the moisture for proper operation and wastage of copies during starting are accordingly unwarranted.

In addition to the advantages stated in the immediately foregoing paragraph, it has been discovered as a part of the present invention, that thinness of the surface coatings alone, regardless of the filler content, contribute very directly to the moisture retaining properties of the printing plate surface. This seems to be due to the fact that thinner printing surface coatings are, to an important degree, less susceptible to picking and cracking, and hence do not offer the serious problems in forming a strong bond with the under layer which are noticeable with thicker surface coatings. Since it is found that the bonding power of an undercoating is in most cases substantially a direct function of its porosity and hence its moisture absorbency, the thinner printing surface coating, by being more nearly indifferent to this factor, permits the use of undercoatings of much less absorbency and more nearly impervious to water. Under the circumstances where such an undercoating is usable, the moisture can be held for much longer periods at the printing face without draining off into or through the undercoating.

In applying the principles of the invention as stated thus far to the preparation of planographic printing plates having a printing coating of carboxymethyl cellulose, the desirable reduction of filler percentages was found to come into conflict with the best method previously known for rendering the layer insoluble as disclosed in the said application of Douglas A. Newman, Serial No. 637,088, now Patent No. 2,655,864, for the aftertreatments of the coating are found to rely to some extent on the filler percentage to permit transmission of the treating solutions fully to all parts of the coating.

According to the present invention it has been discovered that high filler ratios need not be the only manner of reaching the desired result of thoroughly treating all parts of a carboxymethyl cellulose layer with the best salt solutions or insolubilizing factors for producing a high quality printing surface. It has been discovered that it is possible to include in the coating solution ammoniacal copper sulphate as the essential coagulant which will insolubilize the layer when dried and heated to drive off any remnant of ammonia. It has also been discovered that, even though a neutral or slightly alkaline pH must be maintained to keep the copper sulphate in solution, ammonium dichromate and ferric ammonium citrate will also stay in solution and produce suitable iron and chromium reactions with the carboxymethyl cellulose present. These salts, by being dispersed evenly throughout the coating cause the same to coagulate fairly uniformly when dried without necessitating a high permeability, or the high filler content which is a concomitant of such high permeability. In cases where it is also desirable to have the aluminum carboxymethyl cellulose compound make up a portion of the layer, this may be achieved by using aluminum carboxymethyl cellulose as the starting material for the binding ingredient of the composition. Thus, it is possible to include in the completed insoluble layer, the important copper, aluminum, iron and chromium compounds of carboxymethyl cellulose in the desired proportions, by using a self-insolubilizing application. This makes possible low filler content which in turn makes feasible the desirable thin printing surface layers previously described by improving the tendency towards continuity in the films cast.

Planographic plates which embody the principles and advantages of the present invention are represented by the following examples. In each case a sheet of waterleaf paper or other suitable membrane is treated, if desired with suitable wet strength imparting compositions, e. g. by tub sizing with melamine-formaldehyde or urea-formaldehyde, or, in the case of paper, by including such material in the make-up of the sheet by adding it at the beaters. A coating of a suitable oleophilic waterproofing composition, e. g. a mixture of casein-formaldehyde and latex, is then applied to at least one surface of the sheet if desired. When this coating, if used, is dry, a surface planographic printing coat is applied in an amount sufficient to result in a finished dry layer of between ½ and 6 pounds per ream, or preferably between ½ and 4 pounds per ream. Preferably the sheet is calendered or supercalendered one or more times prior to the application of the surface planographic coat in order that the coating may be more easily applied in a continuous fashion at the very reduced thicknesses required. Preferred compositions are:

Example I

Sodium carboxymethyl cellulose	grams	2
Water	cc	95
5% ammoniacal copper sulphate	cc	40
(Corresponds to 2.05 gms. of dry solids dissolved in 38.91 gms. of water.)		
Glycerine	grams	1
Chromium trioxide, C. P	do	0.5
Ferric ammonium citrate, U. S. P. brown	do	1.0

Example II

Sodium carboxymethyl cellulose	grams	2
Water	cc	90
5% ammoniacal copper sulphate	cc	40
Glycerine	grams	1
Ammonium dichromate, C. P	do	0.75
Ferric ammonium citrate, U. S. P. brown	do	1.0

Example III

Aluminum carboxymethyl cellulose	grams	9
Water	do	221
Clay	do	9
Glycerine	do	2.7
5% ammoniacal copper sulphate	cc	50
(Corresponds to 2.56 gms. of dry solids dissolved in 48.64 gms. of water.)		
Ammonium dichromate, C. P	grams	2.25
Ferric ammonium citrate, U. S. P. brown	do	3.0
Ammonium hydroxide	cc	7.0

Example IV

Sodium carboxymethyl cellulose	grams	2
Water	cc	90
Clay	grams	8
5% ammoniacal copper sulphate	cc	40
Glycerine	grams	1
Ammonium dichromate, C. P	do	0.75
Ferric ammonium citrate, U. S. P. brown	do	1.0

Example V

Sodium carboxymethyl cellulose	grams	2.5
Water	cc	78
Methanol	cc	12
5% ammoniacal copper sulphate	cc	40
Glycerine	grams	1
Ammonium dichromate, C. P	do	1.0
Ferric ammonium citrate, U. S. P	do	1.5
Clay	do	10.0

In each of the foregoing examples the carboxymethyl cellulose compound is arranged to bear a proportion to the liquid constituents which will give a solution suffi-

ciently free-flowing to be readily coatable, i. e. of readily coatable viscosity. For most purposes and considering the usual coating equipment, this will be given by a solution of a carboxymethyl cellulose compound of the order of about one percent to five percent by weight.

It should be understood that the improvements disclosed by the present invention in regard to the self-insolubilizing of the coating in situ are applicable to coatings of much greater weight than those specified as preferred above, especially where the matter of cost is secondary.

Variations and modifications may be made within the scope of the claims and portions of the improvements may be used without others.

We claim:

1. A planographic printing plate for the reception of direct images including those formed by carbon paper, comprising a flexible foundation sheet having an image receptive surface; and a planographic surface coating forming a layer overlying and adherent to said flexible foundation on one side thereof comprising a hydrophilic colloid binder and a filler, said coating being substantially continuous but not in excess of 6 pounds per ream in weight, and the ratio of the weight of said filler to the weight of said binder being not less than and not substantially in excess of the values given by Fig. 2.

2. A planographic printing plate for the reception of direct images including those formed by carbon paper comprising a flexible foundation sheet; a preferentially oleophilic undercoat forming an image receptive surface on a side of said sheet; and a planographic surface coating forming a layer overlying and adherent to said undercoat comprising a hydrophilic colloid binder and a filler, said surface coating being substantially continuous but not in excess of 6 pounds per ream in weight, and the ratio of the weight of said filler to the weight of said binder in said surface coating being not less than and not substantially in excess of the values given by Fig. 2.

3. A planographic printing plate for the reception of direct images including those formed by carbon paper comprising a flexible foundation sheet having an image receptive surface; and a planographic surface coating forming a layer overlying and adherent to said flexible foundation on one side thereof comprising a water insoluble carboxymethyl cellulose compound as a binder, and a filler, said coating being substantially continuous but not in excess of 6 pounds per ream in weight, and the ratio of the weight of said filler to the weight of said binder being not less than and not substantially in excess of the values given by Fig. 2.

4. A planographic printing plate for the reception of direct images including those formed by carbon paper comprising a flexible foundation sheet; a preferentially oleophilic undercoat forming an image receptive surface on a side of said sheet; and a planographic surface coating forming a layer overlying and adherent to said undercoat comprising a water insoluble carboxymethyl cellulose compound as a binder, and a filler, said surface coating being substantially continuous but not in excess of 6 pounds per ream in weight, and the ratio of the weight of said filler to the weight of said binder in said surface coating being not less than and not substantially in excess of the values given by Fig. 2.

5. The method of making a planographic printing plate which comprises applying a planographic surface coating to the surface of a flexible foundation using a composition consisting essentially of a primarily aqueous dispersion of a carboxymethyl cellulose compound of coatable viscosity, and ammoniacal copper sulphate, a chromium compound and ferric ammonium citrate, the ammoniacal copper sulphate being about 1 to 2 times the weight (dry basis) of the ferric ammonium citrate, and the chromium compound being between about ½ and ¾ of the weight of the ferric ammonium citrate, the total weight (dry basis) of said ammoniacal copper sulphate, chromium compound and ferric ammonium citrate being on the order of 1 to 2 times the weight of the dry carboxymethyl cellulose compound; and drying the coating to provide a water insoluble printing surface layer.

6. The method of making a planographic printing plate for the reception of direct images including those formed by carbon paper which comprises applying a planographic surface coating to the surface of a flexible foundation which has an image receptive surface, using a composition consisting essentially of a primarily aqueous dispersion of a carboxymethyl cellulose compound of coatable viscosity, a filler, and ammoniacal copper sulphate, a chromium compound and ferric ammonium citrate, the ammoniacal copper sulphate being about 1 to 2 times the weight (dry basis) of the ferric ammonium citrate, and the chromium compound being between about ½ and ¾ of the weight of the ferric ammonium citrate, the total weight (dry basis) of said ammoniacal copper sulphate, chromium compound and ferric ammonium citrate being on the order of 1 to 2 times the weight of the dry carboxymethyl cellulose compound; said coating being applied so as to form a substantially continuous layer but not in excess of six pounds per ream in weight, and the ratio of the weight of said filler to the weight of said carboxymethyl cellulose compound being not less than and not substantially in excess of the values given by Fig. 2; and drying the coating to provide a water insoluble printing surface layer.

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