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PROCESS FOR CHEMICALLY WATERMARKING
PAPER AND PRODUCT THEREOF

Milton O. Schur, New Haven, Conn., and John H. Gold-
berger, Brevard, N.C., assignors to Olin Mathieson
Chemical Corporation, New Haven, Conn., a corpora-
tion of Virginia

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This invention relates to the application to printable
paper sheets of impregnated translucent identification
marks, characterized as substantially permanent and not
impairing the printing and writing properties of the paper
surface. In addition to other advantages, this invention
enables the accurate placing of translucent marks at the
same desired location on successive cut paper sheets
by a printing or stamping operation carried out with the
use of suitable compositions.

Cut paper sheets provided with the conventional type
of watermark, applied during the papermaking process,
generally carry the watermarked monogram or design
at random locations. The accurate placing in cut sheets
of watermarks applied by the conventional process would
necessarily involve unusual precautions and an increased
proportion of scrap, and is therefore unduly expensive.

Compositions have been known for impregnation of
paper for increasing the transparency thereof and result
in translucent sheets or in sheets having translucent areas.
However, such compositions tend to migrate laterally
through the paper sheet. Attempts to apply designs or
marks on paper by printing such compositions have been
unsuccessful because of one or more of the following dis-
advantages: fuzziness of the impressed design or mark
because of lateral spreading, lack of permanence, and
altering the surface so that it does not readily receive
print or writing.

The principal object of this invention has therefore
been to overcome the above disadvantages by providing
suitable compositions which may be printed or stamped
on paper to result in well-defined marks or designs im-
parting permanent translucency at the desired location,
the surface areas of which retain the capacity of the
untreated portions of the paper to receive writing or
printing impressions.

The foregoing and other objectives have been attained
in accordance with this invention by printing or stamp-
ing designs or marks on paper with the use of liquid com-
positions including two substantially non-volatile ingre-
dients of suitable structure and properties to penetrate
readily from one paper surface to the other, without sub-
stantial lateral migration, and to be retained permanently
by the impregnated cellulose fibers.

The main ingredient is an organic ester or polyester,
of molecular weight of about 300 to 10,000 which at room
temperature or at a temperature not higher than about
65° C. exists as a viscous liquid, for example, having a
viscosity exceeding about 1,000 poises. Linear polyesters
of glycols with aliphatic dicarboxylic acids are effective,
and particularly the linear polyesters, or mixtures thereof,
of glycols having 2 to 4 carbon atoms (ethylene, propylene
and butylene glycols) with the aliphatic dicarboxylic acids
containing 6 to 10 carbon atoms (adipic, pimelic, suberic,
azelaic and sebacic acids). Hydrogenated abietate esters
with ethylene glycol, diethylene glycol or triethylene
glycol, or mixtures thereof are likewise suitable, par-
ticularly the triethylene glycol ester. This first ingredient
constitutes 55 to 90% by weight of the residual fiber
impregnating material.

Useful compositions must also include 10 to 45% by
weight of a non-volatile monomeric organic ester plasti-
cizer, which has a melting point below about 45° C. and

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has a boiling point over 250° C. Highly effective esters
are the glycerol esters of the lower fatty acids, par-
ticularly glycerol triacetate and glycerol tripropionate,
and the esters of abietic acid and of stearic acid with the
lower monohydric alcohol containing 1 to 8 carbon atoms,
particularly the methyl and ethyl esters thereof. Diesters
of phthalic acid with the lower monohydric alcohols are
likewise suitable, particularly the dimethyl, diethyl, di-
propyl, dibutyl, dicyclohexyl and dioctyl phthalates, gen-
erally in lower proportions not exceeding about 25% by
weight because of their high fluidity.

The combination of the high molecular weight ester
and the monomeric ester plasticizer results in a liquid
of suitable fluidity and polarity to accomplish rapid
penetration through the web of paper sheets without
lateral spreading. At the same time, sufficient forces of
attraction exist between the liquid esters and cellulose
so that the impregnated fibers tend to be stable and
substantially permanent.

It is at times convenient to replace a portion, up to
about a half, of the plasticizer component by a polar
volatile organic solvent such as a lower alcohol, ether
or ketone or mixture thereof, including methyl, ethyl,
propyl or isopropyl alcohol, diethyl ether, acetone, or
methyl ethyl ketone.

The following specific examples in accordance with
the invention constitute preferred illustrative composi-
tions, the listed proportions being by weight.

Example	Liquid Ester	Plasticizer	Solvent
1.	72 Polypropylene adi- pate (mol. wt. 6000).	28 glycerol triace- tate.	5 acetone.
2.	75 Polypropylene adi- pate (mol. wt. 6000).	20 glycerol tripro- pionate.	
3.	70 Triethylene glycol hydroabietate.	30 methyl hydro- abietate.	10 ethyl alcohol.
4.	do.....	20 butyl stearate.	
5.	85 Nonaethylene gly- col distearate.	15 dioctyl phthal- ate.	5 methyl ethyl ketone.
6.	do.....	10 dibutyl phthal- ate.	

In examples as above, the liquid ester component may
consist of "Paraplex G-40" (Rohm & Haas), of "Stay-
belite Ester No. 3" (Hercules Powder Co.), or of
"Polyethylene Glycol 400 Distearate" (Glyco Products
Co). The plasticizer of Examples 3 and 4 may consist
of "Hercolyn" (Hercules Powder Co.).

Monograms, numerals or other marks or designs are
readily applied using compositions as described above at
the desired location on paper sheets by conventional
stamping or printing methods, for example by letter press
or offset printing. The edges of the marks or designs are
sharp and well defined and the mark or design is uni-
formly translucent and clearly visible when the sheet is
viewed by transmitted light or by reflected light, when
the sheet is placed upon a dark background. Also, the
surface properties of the marked sheet with respect to
receiving writing or printing are not impaired, writing
and printing inks being received uniformly as intended,
without diffusion beyond the desired area. Furthermore,
paper sheets impressed with translucent marks or designs
produced in accordance with this invention retain such
well-defined marks or designs even after accelerated
storage tests, for example, after heating in air for 16
hours at 110° C. In sheets carrying printed text over the
impressed mark, both the mark and the text are non-
fugitive and color-stable after accelerated tests, as above.

It is noteworthy that one or more of the above require-
ments is not obtainable with the prior art compositions,
such as have been proposed for the transparentizing of
paper. For the most part, such compositions diffuse
laterally beyond the line of application and thus result

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in printed designs having indistinct and fuzzy edges. In accelerated tests, the rate of lateral diffusion is increased so that the design or mark practically disappears. With the use of non-polar or slightly polar compounds such as paraffin, petrolatum, stearic acid and similar compounds, the surface properties are altered so that writing and printing inks are not uniformly received. Highly polar compounds are disadvantageous in being sufficiently hygroscopic to cause localized swelling and puckering of the paper sheet or to effect undesirable spreading of subsequently applied writing or printing inks.

In applying marks or designs in accordance with the invention, it is essential to avoid compositions containing appreciable proportions of volatile solvent beyond about 30% by weight. The use of higher percentages of volatile solvent tends to promote the lateral spreading of the composition to an undesirable extent and after volatilization leads to the formation of voids within the impregnated area and imparts a mottled appearance and impaired distinctness of the design or mark.

Modifications of the above-described illustrative embodiments will be obvious to those skilled in the art, without departing from the spirit and scope of the invention, as defined in the claims.

What is claimed is:

1. The process of marking paper sheets with a permanent colorless translucent design comprising printing on paper sheets a layer of liquid in the shape of the said design, which layer is adapted to penetrate rapidly the web of said sheets substantially without lateral diffusion beyond the periphery of the said design, said liquid consisting essentially of 55 to 90 percent by weight of liquid organic viscous ester having a molecular weight in the range of about 300 to 10,000 and 10 to 45 percent by weight of a monomeric non-volatile liquid organic ester plasticizer having a melting point below 45° C. and a boiling point over 250° C.

2. The process of claim 1, wherein the said viscous ester is a linear polyester of a glycol having 2 to 4 carbon atoms with an aliphatic dicarboxylic acid having 6 to 10 carbon atoms.

3. The process of claim 1, wherein the said ester plasticizer is a glycerol ester of a lower fatty acid.

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4. The process of claim 1, wherein the said ester plasticizer is a lower monohydric alcohol ester of an acid selected from the group consisting of abietic, phthalic and stearic acids.

5. The process of claim 1, wherein the said viscous ester is polypropylene adipate and the said ester plasticizer is glycerol triacetate.

6. A paper sheet having a substantially permanent colorless translucent design impregnated in the web thereof, said web being impregnated within the periphery of said design with a liquid composition consisting essentially of 55 to 90 percent by weight of a liquid organic viscous ester having a molecular weight in the range of about 300 to 10,000 and 10 to 45 percent by weight of a monomeric non-volatile liquid organic ester plasticizer having a melting point below 45° C. and a boiling point over 250° C.

7. A paper sheet in accordance with claim 6, wherein the said viscous ester is a linear polyester of a glycol having 2 to 4 carbon atoms with an aliphatic dicarboxylic acid having 6 to 10 carbon atoms.

8. A paper sheet in accordance with claim 6, wherein the said ester plasticizer is a glycerol ester of a lower fatty acid.

9. A paper sheet in accordance with claim 6, wherein the said ester plasticizer is a lower monohydric alcohol ester of an acid selected from the group consisting of abietic, phthalic and stearic acids.

10. A paper sheet in accordance with claim 6, wherein the said viscous ester is polypropylene adipate and the said ester plasticizer is glycerol triacetate.

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MURRAY KATZ, *Primary Examiner*.

H. W. MYLIUS, *Assistant Examiner*.