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SAFETY PAPER

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The present invention relates to the manu-
facture or preparation of improved safety papers,
that is to say of papers mainly used for com-
mercial and legal documents, cheques, bank
notes, bonds and the like, the paper being so
treated as to prevent writing or printing thereon
from being successfully tampered with.

It is known to employ chemically treated pa-
pers for the prevention of tampering, the chem-
icals used for such treatment being selected so
as to give visible stains in contact with ink-
eradicating agents. It has also been proposed
to employ papers treated with fluorescent sub-
stances so that unauthorized alterations or the
like, although not detectable in ordinary daylight,
are made visible by inspecting the document un-
der filtered ultra-violet light. In British speci-
fication 292,393 it is proposed to use for such
treatment of paper a water-soluble fluorescent
salt, namely the sodium salt of 2-naphthol-3:6-
disulphonic acid. The fluorescent substance de-
scribed in the said specification has the disad-
vantage that the surface fluorescence produced
by it in the paper is susceptible to destruction
by water alone. It is therefore possible for the
"cheque raiser" or forger first to extract the
fluorescent substance from the paper with wa-
ter, make unauthorized alterations to the printed
or written document and thereafter restore the
document to its normal appearance by re-treating
it with a suitable fluorescent aqueous solution. To
overcome this disadvantage a further improve-
ment was proposed in British specification
417,488 whereby the fluorescent agent incorpo-
rated in or applied to the paper was to be a wa-
ter-insoluble compound, such as fluorine or
acridine, in the form of a suspension.

There are, however, disadvantages in the use
of water-insoluble fluorescent compounds for
such purposes. In general it is necessary to use
relatively large amounts of suspensions of such
compounds in order to obtain the desired degree
of fluorescence unless extremely highly dispersed
suspensions are used. Such dispersions are
troublesome to make, liable to be unstable, or
flocculated by other chemicals used in the pre-
paration or finishing of paper so that uniform
incorporation or surface application is made dif-
ficult. We have found that the disadvantages
of the known processes can be overcome by the
use of certain fluorescent compounds as herein-
after defined which are water-soluble but which,
because of their strong affinity for cellulose, are
extremely difficult to remove from papers to
which they have been applied.

According to the present invention we in-
corporate into paper or apply superficially to it
the free acid or a water-soluble salt of 4:4'-di-
benzoylamino stilbene-2:2'-disulphonic acid (see
Stobbe and Mallison, Ber. der deutschen Chem.
Gesellschaft, 1913, 46, 1235) or a substitution
derivative thereof. As substitution derivatives
we may use, for example, 4:4'-di-p-aminoben-
zoylamino stilbene-2:2'-disulphonic acid, 4:4'-
di-o-chlorobenzoylamino stilbene-2:2'-disulphon-
ic acid, 4:4'-di-p-methylbenzoylamino stilbene-
2:2'-disulphonic acid. The compounds for use
according to the invention are readily made by re-
acting the appropriate aroyl halides with the
sodium salt of 4:4'-diamino stilbene disulphonic
acid in aqueous medium in the presence of a
mineral acid binding agent, for example, sodium
acetate or sodium carbonate.

The present invention may be carried into ef-
fect in a variety of ways. The said water-solu-
ble fluorescent compounds as already mentioned
have, although substantially colourless, a marked
affinity for cellulose, for example paper pulp,
on which they may be "dyed" by the methods
customary in applying direct dyestuffs to cotton.
By virtue of these properties the said compounds
may be incorporated into the texture or felting
of a paper during manufacture. Thus paper pulp
may be "dyed" with the said fluorescent com-
pounds prior to the formation of a paper or pulp
so "dyed" may be applied superficially to a layer
of "undyed" pulp during the manufacture of a
paper. Alternatively, a pre-formed paper may
be "dyed" by immersion in an aqueous solution
of the said compounds. Where the invention is
carried into effect by "dyeing" a pulp or paper
it has been found that less than 0.5%, generally
about 0.1% by weight of the fluorescent com-
pound in relation to the weight of cellulose ma-
terial to be "dyed" is sufficient to obtain satis-
factory fluorescence. In another embodiment of
the invention an aqueous solution of the said
fluorescent compounds may be applied superfi-
cially to paper by spraying, brushing or printing.

Papers treated according to the invention
fluoresce with a bluish hue when exposed to
filtered ultraviolet radiations, whereas if sub-
jected in parts to the action of ink bleaching
chemicals such as calcium hypochlorite, per-
manganate, and oxalic acid or the like, or, pro-
vided a superficial coating of the stilbene deriva-
tive has been applied, if subjected to the action of
an ink eraser, such localized treatment is im-
mediately apparent under the ultraviolet lamp,
the parts so treated ceasing to fluoresce and ap-

pearing dark against a bluish ground. Thus attempts to eradicate or alter writing on paper treated according to the invention are readily detected. Further, the fluorescent compounds used as indicators of such tampering are not readily removed from the safety papers by contact with water.

The following examples illustrate but do not limit the invention. The parts are by weight.

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Example 1

A solution of 0.1% strength of p:p'-diamino-4:4'-dibenzoyldiamino-stilbene-2:2'-disulphonic acid sodium salt is applied to the surface of paper at a convenient part of a paper machine by means of a water doctor or spray in the well known manner. The paper is dried as usual on the drying rolls which follow the said convenient part. If desired the stilbene sulphonic acid derivative can be applied to the paper pulp in the beater but since the whole body of the paper will then be impregnated with the sulphonic acid, it will not be so sensitive to surface erasures, but will be equally sensitive to bleaching chemicals which penetrate through the paper.

Example 2

Sufficient of the same stilbene compound as used in Example 1 is added to a 2% solution of gelatine, glue or casein to make a 0.1% solution of the stilbene sulphonic acid derivative which is then applied to the surface of the paper by brushing, dipping, spraying or printing. Drying is effected in any convenient manner.

We claim:

1. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 4:4'-di-(benzoylamino) stilbene 2:2'-di-sulfonic acid compound.
2. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein an alkali metal salt of a 4:4'-di-(benzoylamino) stilbene 2:2'-disulfonic acid compound.
3. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 4:4'-di-(aminobenzoylamino) stilbene 2:2'-di-sulfonic acid compound.
4. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein an alkali metal salt

of a 4:4'-di-(benzoylamino) stilbene 2:2'-disulfonic acid.

5. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein an alkali metal salt of a 4:4'-di-(aminobenzoylamino) stilbene 2:2'-disulfonic acid.

6. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein an alkali metal salt of 4:4'-di-(p-amino-benzoylamino) stilbene 2:2'-disulfonic acid.

7. Paper and the like having incorporated therein a 4:4'-di-(benzoylamino) stilbene 2:2'-disulfonic acid compound.

8. Paper and the like having incorporated therein an alkali metal salt of a 4:4'-di-(benzoylamino) stilbene 2:2'-disulfonic acid compound.

9. Paper and the like having incorporated therein an alkali metal salt of a 4:4'-di-(aminobenzoylamino) stilbene 2:2'-disulfonic acid.

10. Paper and the like having incorporated therein an alkali metal salt of a 4:4'-di-(benzoylamino) stilbene 2:2'-disulfonic acid.

11. Paper and the like having incorporated therein an alkali metal salt of 4:4'-di(p-amino-benzoylamino) stilbene 2:2'-disulfonic acid.

12. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein the sodium salt of 4:4'-di-(p-amino-benzoylamino) stilbene 2:2'-disulfonic acid.

13. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein 4:4'-di-o-chlorobenzoylamino stilbene 2:2'-disulfonic acid.

14. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein 4:4'-di-p-methylbenzoylamino stilbene 2:2'-disulfonic acid.

15. Paper and the like having incorporated therein the sodium salt of 4:4'-di(p-amino-benzoylamino) stilbene 2:2'-disulfonic acid.

16. Paper and the like having incorporated therein 4:4'-di-o-chlorobenzoylamino stilbene 2:2'-disulfonic acid.

17. Paper and the like having incorporated therein 4:4'-di-p-methylbenzoylamino stilbene 2:2'-disulfonic acid.

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