CONVENTION APPLICATION FOR A PATENT

Coates Brothers & Company Limited

of Easton Street, Rosebery Avenue, London WC1 ENGLAND,

hereby apply for the grant of a Patent for an invention
etitled: "PRINTING INKS"

which is described in the accompanying complete specification.

This application is a Convention application and is based on the
application(s) numbered: 5781/77

for a patent or similar protection made in GREAT BRITAIN

on 11th February, 1977.

Our address for service is care of Griffith, Hassel & Frazer,
Patent Attorneys, of 323 Castlereagh Street, Sydney 2000, in the
State of New South Wales, Commonwealth of Australia.

DATED this 9th day of February, 1978.

COATES BROTHERS & COMPANY LIMITED
By their Patent Attorney,

of Griffith, Hassel & Frazer
Fellows, Institute of Patent
Attorneys of Australia
COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1960

DECLARATION FOR CONVENTION PATENT APPLICATION

(Note: (1) To be signed by the applicant(s), if individual(s). If applicant is a Company, to be signed by a person or its behalf. (2) This is a comprehensive form, and parts inappropriate to a particular application should be cancelled.)

COMMONWEALTH OF AUSTRALIA

DECLAREATION IN SUPPORT OF A CONVENTION APPLICATION

FOR A PATENT OR PATENT OF ADDITION

In support of the Convention application No. (a)

made by (b) COATES BROTHERS & COMPANY LIMITED

for a patent/patent of addition for an invention entitled (c) "Printing Inks"

1. I am/We are the applicant(s) for the patent/patent of addition (or, in the case of an application by a body corporate) authorized by the abovementioned applicant(s) for the patent/patent of addition to make this declaration on their behalf.

2. The basic application(s) as defined by Section 141 of the Act was/were made in the following country or countries on the following date(s) by the following applicant(s) namely:

   in (f) Great Britain on (g) 11th February 1977
   by (h) COATES BROTHERS & COMPANY LIMITED

3. I/We are the actual inventor(s) of the invention (or, where a person other than the inventor is the applicant)

   of (j) 133, Highview, Meopham, Gravesend, Kent, England

   is/are the actual inventor(s) of the invention and the facts upon which the applicant(s) is/are entitled to make the application are as follows:

   (k) The Applicants are the Assignees of the Invention from the actual Inventor.

4. The basic application(s) referred to in paragraph 2 of this Declaration was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

Declared at LONDON this 30th day of JANUARY 1978

To: The Commissioner of Patents, Commonwealth of Australia.
The inks are said to be particularly suitable for printing onto a polyolefin substrate.

CLAIM

1. A printing ink containing, as ink binder, a solution of (1) a carboxy group-containing copolymer of ethylenically unsaturated monomers, (2) an epoxy resin and (3) an aminoalkyl-siloxane curing agent, in a solvent therefor.
The following statement is a full description of this invention, with the best method of performing it known to me/us:-
This invention is concerned with improvements in or relating to printing ink compositions and methods of printing employing such compositions. The invention is particularly concerned with compositions suitable for printing upon polymeric substrates, especially polyolefin substrates.

Polymeric substrates, especially polyolefin substrates, are notably difficult to print upon in order to obtain a good, well adhering image on the substrate.

It has now been found, in accordance with the present invention, that a suitable composition for printing upon a polymeric substrate comprises, as ink binder, a solution of (1) a carboxy-group containing copolymer of ethylenically unsaturated monomers, (2) an epoxyresin and (3) amino-alkyl siloxane curing agent and, accordingly, the invention provides, in accordance with one aspect thereof a printing ink having an ink binder as defined above. The invention also provides a method of printing upon a substrate, particularly a polymeric substrate such as a polyolefin substrate (e.g. a polyethylene or polypropylene substrate) a printing ink having an ink binder as defined above. Such printing is preferably effected by a flexographic or gravure process.

The printing inks of the invention comprise as one principal component, a carboxy-group containing copolymer derived from two or more ethylenically unsaturated monomers. Such copolymers will
generally be derived from an ethylenically unsaturated carboxylic acid, such as acrylic or methacrylic acid, and one or more ethylenically unsaturated monomers copolymerizable therewith such as vinyl hydrocarbons, e.g. styrene or an alkyl styrene, or esters of ethylenically unsaturated carboxylic acids such as alkyl or cycloalkyl esters of acrylic or methacrylic acid.

Preferably the carboxyl group-containing copolymer will have an acid value of from 20 to 80 mg/KOH/g since acid values above this range may give rise to compatibility problems with the epoxy resin component of the ink binder and values below this range may give prints having less satisfactory resistance properties.

The component monomers of the copolymer, other than the unsaturated carboxylic acid, and their relative proportions may be chosen to provide the resultant polymer with the desired degree of flexibility as is well known in the art. Thus, for example, styrene and methyl methacrylate yield hard brittle polymers whilst butyl acrylate yields soft flexible polymers. A mixture of, for example, methyl methacrylate and butyl acrylate yields a polymer of intermediate flexibility and hardness. Accordingly, the nature and relative proportions of the other comonomer(s) may be chosen to give a polymer having the desired properties as required for any particular application.

The carboxy group-containing copolymers may be prepared by any suitable polymerization technique applicable to the preparation of
copolymers from ethylenically unsaturated monomers but are preferably prepared by solution polymerization in the presence of a free radical catalyst such as an organic peroxide.

The second principal component of the ink binder is an epoxy resin or polyepoxide, i.e. an organic compound containing two or more epoxy groups. Typical epoxy resins are glycyl ethers of polyhydric alcohols or phenols derived from the reaction of the alcohol or phenol with a halohydrin, e.g. epichlorohydrin, in the presence of an alkali.

Such epoxy resins may be represented by the general formula:

\[
\begin{align*}
\text{CH}_2 &- \text{CH} - \text{CH}_2 \text{O} \{ \text{R} - \text{O} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{O} \}_n \text{ - R} - \text{O} - \text{CH}_2 - \text{CH} - \text{CH}_2 \\
\text{OH} &
\end{align*}
\]

in which \( n \) is 0 or an integer from 1 to 20 and \( R \) is a divalent organic radical. As will be understood the epoxy resin may, depending upon the condition of its preparation, contain one or more species of the above formula.

A particularly preferred class of epoxy resins are those in which \( R \) represents a group:
Other suitable epoxy resins are those derived from a phenol/formaldehyde novolak resin and a halohydrin and which may be represented by the general formula:

\[
\begin{align*}
\text{in which } m &\text{ is 0 or an integer from 1 to 5 and } R^1 \text{ is a hydrogen atom or an alkyl group-containing from 1 to 4 carbon atoms. Again, it will be understood that, depending upon the conditions of their preparation such epoxy resin may contain one or more species of the above formula.}
\end{align*}
\]

The weight ratio of carboxy group-containing polymer to epoxy resins is suitably from 3:1 to 1:3, preferably from 2:1 to 1:2.

The third component of the ink binder is an aminoalkyl siloxane curing which may be represented by the formula:

\[
\begin{align*}
\text{in which } R^2 \text{ and } R^3 \text{ are the same or are different and each is a lower alkylene group (for example containing from 1 to 6 carbon atoms) and } R^4 \text{ is a lower alkyl group (for example containing from 1 to 4 carbon atoms).}
\end{align*}
\]

Examples of such curing agents are γ-aminopropyl-triethoxysilane and N-(β-amoethyl)-γ-aminopropyl trimethoxysilane.

The weight ratio of curing agent to carboxy group-containing copolymer and epoxy resin is suitably from 1:3 to 1:5.
The printing ink of the invention will also comprise a solvent for the resin binder system and such solvent can comprise a lower alkyl ester of a lower fatty acid, e.g. ethyl acetate, alone or in admixture with other solvents such as, for example, aromatic hydrocarbons such as toluene or lower alkanols, such as industrial methylated spirit.

The printing ink will also generally comprise a pigment or colouring agent and such may comprise an inorganic pigment or organic pigment or dyestuff.

It is a particular advantage of the printing ink compositions of the invention that they do not require additional heat to cure them. In other words they are printed upon the desired substrate, the solvent is allowed to evaporate off to give a tack free print, and the printed substrate rolled up for storage, during the course of which storage curing of the resin/curing agent system takes place to form an adherent, resistant print upon the substrate. It will, accordingly, be appreciated that the printing ink composition comprising the carboxy group-containing copolymer, epoxy resin and curing agent is inherently unsuitable for storage for periods of more than a few hours. Accordingly, the printing ink compositions of the invention will generally be presented as two-part packages, the first package comprising the carboxy group-containing copolymer and the epoxy resin and the second package containing the
curing agent. Other ingredients (such as pigments and solvents) of the composition may be included in either or both of the packages but are preferably included in the first package, the second package consisting essentially of curing agent.

In order that the invention may be well understood, the following Example is given by way of illustration only.

**EXAMPLE**

A printing ink composition, suitable for use in flexographic or gravure processes, was prepared by dissolving

A. COOH copolymer * & Epikote 1001 12 parts by weight 17 parts by weight 29

in

B. Toluene 12 parts by weight

Industrial Methylated Spirits (74 OP) 12 parts by weight

Ethyl Acetate 12 parts by weight 36

using a laboratory model high speed dissolver.

*A copolymer of methyl methacrylate, ethyl acrylate and methacrylic acid in a mole ratio of 4.5 : 3 : 1 having a viscosity (as a 30%, solution in industrial methylated spirit/ethyl acetate) of 100 cps at 25°C.*
35 Parts by weight rutile titanium dioxide (Bayer Titan RFD 1) were added and dispersed in the solution using the dissolver until an Ault and Wiborg grind gauge reading less than 0.1 thou had been achieved.

This pigment dispersion was mixed with N,β (aminoethyl) γ (aminopropyl) trimethoxy silane in a weight ratio of 12 : 1.

Finally the composition was thinned to application viscosity with 2 : 1 by weight mixture of Industrial methylated spirits and ethyl acetate (23-30 secs Zahn Cup No. 2).

This ink was printed on Shorko SCC film using a 12" laboratory model Moser press at a web speed of 300 ft/minute and a drying temperature of 75°C.

Adhesion of the print was tested after 20 minutes using the Scotch tape test:

the print remained intact.

The ink was found to be non-blocking and the print was very glossy.
After 3 days at room temperature in the reel the solvent resistance of the print was examined by wiping gently with an isopropyl acetate soaked piece of cotton wool. The print had a resistance of greater than 50 wipes.

The heat resistance of the printed ink was determined using a Sentinel Heat Sealer, set at 20 p.s.i. and a 2 second dwell time. The face-to-face resistance was found to be greater than 165°C (the heat distortion temperature of the Shorko film); The face-to-foil heat resistance was also greater than 165°C.

After three days in the reel the grease resistance of the print was tested by applying corn oil to the surface of the print and allowing it to stand at room temperature for 10 minutes. The print/corn oil composite was subjected to twenty rubs between the thumb and forefinger of each hand. The print exhibited the exceptional result of no ink removal when subjected to this treatment. (A conventional ink would be expected to exhibit up to 50% removal of the print under these conditions.

The same ink formulation was run on commercial packaging machinery both of the vertical form filled seal (vffs) and horizontal form filled seal (hffs) types. No marking of the print, ink removal or smearing was noted in the heat seal area.
The claims defining the invention are as follows:

1. A printing ink containing, as ink binder, a solution of (1) a carboxy group-containing copolymer of ethylenically unsaturated monomers, (2) an epoxy resin and (3) an aminoalkyl-siloxane curing agent, in a solvent therefor.

2. A printing ink as claimed in claim 1 in which the carboxy group-containing copolymer is a copolymer of acrylic or methacrylic acid and a vinyl hydrocarbon and/or an ester of an ethylenically unsaturated acid.

3. A printing ink as claimed in claim 1 or claim 2 in which the carboxy group-containing copolymer has an acid value of from 20 to 80 mg KOH/g.

4. A printing ink as claimed in any one of the preceding claims in which the epoxy resin is the reaction product of a polyhydric alcohol or phenol and a halohydrin.

5. A printing ink as claimed in claim 4 in which the epoxy resin comprises one or more species of the formula;
in which $n$ is 0 or an integer from 1 to 20 and $R$ is a divalent organic radical.

6. A printing ink as claimed in claim 5 in which $R$ represents a group

7. A printing ink as claimed in any of claims 1 - 3 in which the epoxy resin is the reaction product of a phenol/formaldehyde novolak resin and a halohydrin.

8. A printing ink as claimed in claim 7 in which the printing ink comprises one or more species of the formula:
in which \( m \) is 0 or an integer from 1 to 5 and \( R^1 \) is a hydrogen atom or an alkyl group containing from 1 to 4 carbon atoms.

9. A printing ink as claimed in any one of the preceding claims in which the weight ratio of carboxy group-containing copolymer to epoxy resin is from 3 : 1 to 1 : 3.

10. A printing ink as claimed in claim 9 in which the said ratio is from 2 : 1 to 1 : 2.

11. A printing ink as claimed in any one of the preceding claims in which the weight ratio of curing agent to carboxy group-containing copolymer and epoxy resin is from 1 : 3 to 1 : 5.

12. A printing ink as claimed in any one of the preceding claims in which the solvent comprises a lower alkyl ester of a lower fatty acid.

13. A printing ink as claimed in claim 12 in which the ester is ethyl acetate.

14. A printing ink as claimed in claim 1 substantially as hereinbefore described with reference to the Example.
15. A two-part pack for the preparation of an ink as claimed in any one of the preceding claims comprising a first package containing the carboxy group-containing copolymer and the epoxy resin and a second package containing the curing agent, either or both of said packages also containing the solvent.

16. A two-part pack as claimed in claim 15 in which the second package contains only the curing agent.

17. A method of printing a substrate which comprises printing the substrate with an ink as claimed in any one of claims 1 - 14.

18. A method as claimed in claim 17 in which the substrate is a polyolefin substrate.

19. A method as claimed in claim 17 or claim 18 in which printing is effected by a flexographic or gravure process.

20. A method as claimed in claim 17 substantially as hereinbefore described with reference to the Example.

DATED this 9th day of February, 1978.

COATES BROTHERS & COMPANY LIMITED
By their Patent Attorney,
of GRIFFITH, HASSEL & FRAZER.