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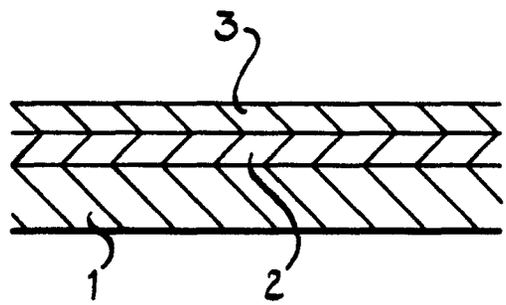
(54) Light-sensitive vesicular recording material.

(57) Light-sensitive vesicular imaging materials, suitable for the production of coloured labels etc, comprise a light-sensitive vesicular imaging layer (2) applied to one surface of a transparent self-supporting plastics sheet or film (1), said light-sensitive vesicular imaging layer comprising a polymeric vehicle having uniformly dispersed therein a sensitising agent which releases a vesicle-forming gas upon exposure to light, said polymeric vehicle comprising a thermoplastic polymer having a nitrogen permeability constant in the range 1×10^{-15} to 1×10^{-10} and being softenable upon heating above ambient temperature to permit the gas released by the sensitising agent in the light-struck areas to form light-scattering or reflecting vesicles therein, wherein at least one pigmented or dyed coating layer (3) having an opacity represented by a total luminous transmittance measured by ASTM test method D-1003-61 not exceeding 25% is applied over the vesicular imaging layer (2) and remote from the plastics sheet or film (1).



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TITLE MODIFIED
see front page

RECORDING MATERIALS

The present invention relates to a light-sensitive vesicular imaging material.

Vesicular imaging materials are known and generally comprise a film or sheet support carrying an imaging layer comprising a plastics vehicle and a sensitising agent dispersed through the vehicle. The sensitising agent is decomposable on exposure to actinic light to evolve a gas such as nitrogen thereby forming a latent gas image in the vehicle. Generally, the latent image may be developed by heating the material, usually above the softening temperature of the plastics vehicle, to enable the gas in the light-struck areas to expand into bubbles or vesicles which have a light-scattering or reflecting activity. British patent specification 861 250 describes such materials and discloses that the support may be opaque and of any desirable colour. Paper and synthetic sheet material supports are mentioned.

According to the present invention a plastics imaging material which comprises an imaging layer comprising a polymeric vehicle in which imaging information can be recorded by the production of gas vesicles therein, applied to one surface of a transparent self-supporting plastics sheet or film, said polymeric vehicle comprising a thermoplastic polymer having a nitrogen permeability constant in the range 1×10^{-15} to 1×10^{-10} and being softenable upon heating above ambient temperature to permit the formation of light-scattering or reflecting gas vesicles therein, wherein at least one pigmented or dyed coating layer having an opacity represented by a total luminous transmittance measured by ASTM test method D-1003-61 not exceeding 25% is applied over the imaging layer and remote from the plastics sheet or film.

More specifically according to the present invention, a light-sensitive vesicular imaging material comprises a

light-sensitive vesicular imaging layer applied to one surface of a transparent self-supporting plastics sheet or film, said light-sensitive vesicular imaging layer comprising a polymeric vehicle having uniformly dispersed therein a sensitising agent which releases a vesicle-forming gas upon exposure to light, said polymeric vehicle comprising a thermoplastic polymer having a nitrogen permeability constant in the range 1×10^{-15} to 1×10^{-10} and being softenable upon heating above ambient temperature to permit the gasreleased by the sensitising agent in the light-struck areas to form light-scattering or reflecting vesicles therein, wherein at least one pigmented or dyed coating layer having an opacity represented by a total luminous transmittance measured by ASTM test method D-1003-61 not exceeding 25% is applied over the vesicular imaging layer and remote from the plastics sheet or film. According to the invention, a pigment or dye may optionally be included in the light-sensitive vesicular imaging layer.

Preferably, a single pigmented or dyed opaque coating is included in the imaging material and provides coloured areas by the absorption of incident light which contrast with records formed as vesicles in the light-sensitive imaging layer, the records therein being viewed essentially by the scattering and reflection of light in the vesicles.

The vesicular imaging materials of this invention may be used for the production of coloured display labels, signs and other products as discussed later, wherein the information recorded in the vesicular imaging layer is viewed against the colouration of the pigmented and dyed layer and the imaging layer is protected from damage by the plastics sheet or film through which the recorded information is viewed. Additional colouring effects may optionally be obtained by applying a transparent pigmented

or dyed layer to the surface of the plastics sheet or film remote from the vesicular imaging layer.

The term "nitrogen permeability constant" used herein refers to the volume of nitrogen in cm^3 which diffuses in one second through one cm of a sample of the polymeric vehicle, one cm^2 in area, and under a pressure gradient of one cm of mercury at a constant temperature of 25°C.

The term "ambient temperature" relates to temperatures of at least 20°C.

The transparent self-supporting plastics sheet or film may consist of any suitable plastics material, which may optionally be coloured by means of a dye, such as cellulose esters, e.g. cellulose acetate, or thermoplastics, such as polystyrene, polyamides, polymers and copolymers of vinyl chloride, polycarbonate, polymers and copolymers of olefines, e.g. polyethylene and polypropylene, polysulphones and linear polyesters which may be obtained by condensing one or more dicarboxylic acids or their lower alkyl diesters, e.g. terephthalic acid, isophthalic, phthalic, 2,5-, 2,6- and 2,7-naphthalene dicarboxylic acid, succinic acid, sebacic acid, adipic acid, azelaic acid, diphenyl dicarboxylic acid, and hexahydroterephthalic acid or bis-p-carboxyl phenoxy ethane, optionally with a monocarboxylic acid, such as pivalic acid, with one or more glycols, e.g. ethylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol and 1,4-cyclohexanedimethanol. Biaxially oriented and heat-set films of polyethylene terephthalate are particularly useful according to this invention.

The polymeric vehicle of the light-sensitive vesicular imaging layer may comprise any of the thermoplastic polymers known in the art for use in vesicular imaging layers and having properties such that light-scattering or reflecting vesicles can be formed therein. Suitable polymeric vehicles include polymers of

vinylidene chloride as described in British patent specification 861 250 and the polymers described in British patent specifications 1 272 894, 1 276 608, 1 278 004, 1 312 573, 1 330 344, 1 352 559, 1 352 560 and 1 400 245.

The light-sensitive vesicular imaging layer may optionally include any of the known additives such as surfactants and stabilising acids.

The sensitising agent incorporated into the vehicle should be non-reactive with the vehicle. Likewise, the vesicle-forming gas which is liberated by the sensitising agent should be non-reactive with the vehicle. The liberation of gas by the sensitising agent for the formation of light-scattering or reflecting vesicles is achieved solely by the action of light upon the sensitising agent; sensitising agents which liberate gas by other mechanisms, e.g. under the influence of heat are not employed according to the present invention. Sensitising agents which liberate nitrogen on exposure to actinic light, especially ultra-violet light which is widely used in vesicular processing equipment, may be employed according to this invention, suitable agents including nitrogen-liberating diazonium salts, such as those which may be derived from the following amines:

N,N-dimethyl-p-phenylenediamine
N,N-diethyl-p-phenylenediamine
N,N-dipropyl-p-phenylenediamine
N-ethyl-N-β-hydroxyethyl-p-phenylenediamine
N,N-dibenzyl-3-ethoxy-4p-phenylenediamine
4-N-morpholino-aniline
2,5-diethoxy-4-N-morpholino-aniline
2,5-dimethoxy-4-N-morpholino-aniline
2,5-di-(n-butoxy)-4-N-morpholino-aniline
4-N-pyrrolidino-aniline

3-methyl-4-N-pyrrolidino-aniline
3-methoxy-4-N-pyrrolidino-aniline
2-ethoxy-4-N,N-diethylamino-aniline
2,5-diethoxy-4-benzoylamino-aniline
2,5-diethoxy-4-thio-(4'-tolyl)-aniline

The imaging layer may be applied to the plastics sheet or film as a solution in any suitable common organic solvent, such as butan-2-one, toluene and methanol, by any of the means known in the art for coating light-sensitive imaging layers.

The imaging layer may optionally be treated with an aqueous solution or steam or water vapour to reduce its contrast or photographic gamma by techniques which are already established in the art, e.g. as described in United States patent specification 3 149 971.

If desired, the surface of the plastics sheet or film may be pretreated and/or coated with an adhesion-promoting layer prior to the application of the imaging layer. Polyethylene terephthalate film carriers may be pretreated by coating with solutions of materials having a solvent or swelling action on the film such as halogenated phenols in common organic solvents, e.g. solutions of p-chloro-m-cresol, 2,4-dichlorophenol, 2,4,6- or 2,4,5-trichlorophenol or 4-chlororesorcinol or a mixture of such materials in acetone or methanol. After application of such a solution the film surface can be dried and heated at an elevated temperature for a few minutes, e.g. 2 minutes at 60° to 100°C. If desired, the pretreating solution may also contain an adhesion-promoting polymer such as a partially hydrolysed copolymer of vinyl chloride and vinyl acetate.

As an alternative to, or in addition to, such a pretreatment, a material having a swelling or solvent action upon the film may be incorporated into the coating composition applied to the film.

Such treatments may also be applied to the surface other than that carrying the vesicular imaging layer to promote adhesion to coating layers which may be applied thereto.

According to the invention, a pigmented or dyed layer is applied over the surface of the light-sensitive imaging layer which may itself optionally be pigmented or dyed itself. The applied pigmented or dyed layer is preferably applied directly to the light-sensitive imaging layer. The pigmented or dyed layer may include a polymeric binder preferably having a nitrogen permeability constant greater than 1×10^{-15} comprising nitrocellulose, cellulose esters such as cellulose acetate, cellulose acetate butyrate and cellulose acetate propionate, copolymers of vinyl chloride and vinyl acetate or copolymers of alkyl esters of methacrylic acid such as methyl and n-butyl methacrylates, styrene/acrylonitrile copolymers, polyamides and any other soluble or dispersible resins conventionally employed in paints and printing inks. Suitable printing inks include those available commercially as 'Impac Microfilm' Black, Pale Blue, Red, Green, Orange and Pink (Fishburn Printing Ink Co Ltd), and 'Propalin Blue' and 'Propalin Red' (both Gothams). Suitable paints include the range of 'Dulux' emulsion paints (Imperial Chemical Industries Limited) especially black, blue, red and green hues.

The pigments and dyes included in the pigmented or dyed coating layer are present solely to provide coloured effects by the absorption of certain wavelengths of incident light employed to view the material. The total luminous transmittance of the pigmented or dyed layer preferably does not exceed 20% and may be as low as zero %. Pigments may be included in the pigmented or dyed coating layer in an amount in the range 5 to 30% by weight based on the weight of the polymeric binder and may be

chosen from carbon black or those identified by the Colour Index names or numbers (the commercially available pigments are named in parenthesis) 74160 (Polymon Blue LBS), 15850 (Rubine Toner 4BS), Pigment Yellow 34 (Pure Lemon Chrome L6GS), 69800 (Paliogen Blue RR) and Azoic Blue 7 (Printing Blue R). Dyes may be included in the coating layer in an amount in the range 5 to 30% by weight based on the weight of the polymeric binder and may be chosen from those identified by the Colour Index names or numbers (the commercially available dyes are named in parenthesis) Solvent Blue 70 (Neozapon Blue FLE), Solvent Red 60 (Neozapon Fire Red BL), 12716 (Neozapon Red GE), Solvent Blue 49 (Orasol Blue BLN), Solvent Blue 53 (Orasol Navy Blue 2RB), Solvent Blue 67 (Orasol Brilliant Blue GN), 12055 (Lacquer Orange VG), Solvent Blue 65 (Waxoline Blue 2RS), 61551 (Waxoline Blue APS), 60505 (Waxoline Red MPS), 47000 (Waxoline Yellow TS) and 50415 (Methasol Nigrosine ENS).

The pigmented or dyed coating layer may also contain a resin which confers self-adhesive or pressure-sensitive adhesive properties upon the layer thereby enabling the imaging material to be bonded to receptive substrates.

Alternatively, a self-adhesive or pressure-sensitive adhesive layer may be applied to either side of the material, but preferably to the same side as that carrying the vesicular imaging layer since the latter will be protected by the plastics sheet or film from damage by abrasion when adhered to a receptive substrate. Resins suitable for the formation of such an adhesive layer are described in "Handbook of Adhesives" edited by I Skeist, Rheinhold Pub Corp, New York, 1962 and may include copolymers based on aliphatic (4-12 carbon atoms) acrylate esters, e.g. iso-octyl acrylate copolymers, natural and/or synthetic rubber-based copolymers blended with a "tackifying component such as a polyterpene and styrene/butadiene rubbers".

A peelable backing layer such as a paper sheet coated with a release layer may be applied over the adhesive layer to prevent premature adhesion to other surfaces.

An alternative means for applying the adhesive layer and peelable backing is by dry transfer lamination of a double-side coated adhesive tape having a peelable backing on one side only. There are many tapes suitable for this purpose on the market such s 3M's Y972 and 463, Fasson's 6321 and Tivolikay's 571 transfer tapes.

The imaging materials according to this invention may be exposed to a light image in a conventional manner to produce a latent image in the recording layer. The image may be developed in a conventional manner by heating immediately after light exposure to permit the gas vesicles to form in the light-struck areas. Fixing may then be accomplished if desired by a futher overall light exposure and permitting the gas evolved by the decomposition of the sensitising agent to diffuse out of the recording layer. Alternatively, the latent image may be reversal processed by permitting the gas evolved in the imagewise light-struck areas to diffuse out of the recording layer and then subjecting the material to an overall light exposure followed by immediate heating to form gas vesicles in the areas subjected to the overall exposure.

The invention is further described with reference to certain preferred embodiments thereof which are illustrated by the accompanying drawings, in which:

Figure 1 is a cross-section of an imaging material having a vesicular imaging layer and a pigmented layer;

Figure 2 is a cross-section of a modification of the imaging material illustrated in Figure 1 and including an adhesive layer applied over the pigmented layer; and

Figure 3 is a cross-section of a modification of the imaging material illustrated in Figure 2 and including a peelable backing paper.

The light-sensitive vesicular imaging material illustrated in Figure 1 comprises a conventional biaxially oriented and heat-set undyed transparent polyethylene terephthalate film 1 of thickness 125 microns. The upper surface of the film 1 was pretreated prior to coating with a light-sensitive imaging layer 2 with a solution of 2.0 g p-chloro-m-cresol in 100 ml of methanol and dried by heating at 120°C for 2.5 minutes. The imaging layer 2 includes a polymeric vehicle consisting of a copolymer of 85 mole % vinylidene chloride and 15 mole % acrylonitrile which has a nitrogen permeability constant of 0.5×10^{-13} and a diazonium salt sensitising agent present in an amount of 10% by weight based upon the weight of the polymeric vehicle. The imaging layer 2 was applied from a lacquer of the following formulation:

Ingredients	Quantities
Copolymer of vinylidene chloride and acrylonitrile	80 g
Polymethyl methacrylate	20 g
Phthalic acid	2 g
4-N-morpholino-2,5-diethoxybenzene diazonium borofluoride	8 g
Butan-2-one	1000 ml

and dried to a dry thickness of about 6 microns by heating at 120°C to 130°C.

An opaque pigmented layer 3 is adhered to the imaging layer 2 and was produced by the application of an ink which is commercially available as 'Impac Microfilm' Black from Fishburn Printing Ink Co Ltd (analysis black pigment and polymeric binder in a solvent mixture of ethanol and ethyl acetate). The ink was dried by heating at 80°C to provide a layer having a dry thickness of about 6 microns and a total luminous transmittance measured by ASTM test method D-1003-61 of zero %.

Figure 2 relates to a modification of the imaging material illustrated in Figure 1 and includes an adhesive layer 4 bonded to the pigmented layer 3. The adhesive layer 4 includes a self-adhesive or pressure-sensitive adhesive resin comprising a self-curing acrylic polymer which was applied from a composition comprising:

Ingredients	Quantities
Self-curing acrylic polymer commercially available as 'Gelva' RA1753 (analysis: 31% by weight solids in a solvent mixture comprising by volume 55% ethyl acetate, 35% isopropanol and 10% hexane)	50 ml
Ethyl acetate	50 ml

and dried to a dry thickness of about 25 microns by heating at 80°C for 20 seconds.

Figure 3 relates to a modification of the imaging material illustrated in Figure 2 and includes a peelable backing paper 5 adhered to the adhesive layer 4 to protect the latter against unintentional premature bonding to other surfaces. The peelable backing paper 5 is of conventional construction and comprises a release coating applied to its surface adjacent the adhesive layer 4.

In further modifications of the materials illustrated in Figures 1 to 3, the light-sensitive imaging layer 2 also includes a commercially available red dye Savinyl Fire Red GLS which was added to the lacquer formulation used to apply layer 2 in an amount of 4.2% by weight based upon the weight of the polymeric vehicle.

In other modifications of the materials illustrated in Figures 1 to 3, the film 1 is coloured by means of a dye.

Other modifications of the materials illustrated in Figures 1 to 3 include a dye substituted for the pigment in the layer 3.

Depending upon the nature of the imaging material employed and the choice of normal or reversal processing for the light-sensitive imaging layer it is possible to produce a variety of colourful and attractive imaged products. For example, when the material illustrated in Figure 1 is processed normally, the processed image appears as a white vesiculated image in the light-struck areas upon a coloured background represented by the pigmented layer 3. On the other hand, if the same material is reversal processed the image has the colour of the pigmented layer 3 upon a white vesiculated background.

It will be appreciated that the imaging and processing operations are not complex. Thus, whilst imaging can be achieved by exposure to an ultra-violet light source, an alternative procedure is simply to expose the material to sunlight. Processing by heating, depending upon the nature of the imaging layer, can be achieved at temperatures of 60° to 160°C, by immersion in hot liquids, e.g. boiling water, hot plates, e.g. domestic irons, and commercially available vesicular developers such as Kal Developer 360VS (Canon Inc). Accordingly, the materials of the present invention may be used in many industrial, commercial and domestic applications for the production of display labels and signs, etc. Multiple copies of the same master image can be produced by repeating the exposure and processing operations.

Exposure to actinic light is preferably achieved by exposing the light-sensitive imaging material through a master image whilst held firmly in contact with the master image, although exposure by projection is possible.

Master images may be supported on transparent film or even paper. For example, the master image may comprise a photographic silver halide master, or may be constructed by drawing, dry transfers, printing, typing, electrostatic photocopying and/or montage techniques.

The light-sensitive vesicular imaging materials of this invention may be imaged as described above to produce labels, signs, business cards, toy products, drafting proofing materials, engineering drawing, engineering drilling patterns when applied by an adhesive to the workpiece, identification tags, name plates, instruction panels, warning plaques, badges, instrument panels, dial faces, circuit diagrams, duplicate certificates, printed circuit board component designation, identity cards, security cards, control panels, direction indicators, print proof film for photographic silver halide camera films, name plates, face plates, lubrication charts, operating procedures, gauge labels, trademarks and tags, and menu cards.

CLAIMS

1. A plastics imaging material which comprises an imaging layer comprising a polymeric vehicle in which imaging information can be recorded by the production of gas vesicles therein, applied to one surface of a transparent self-supporting plastics sheet or film, said polymeric vehicle comprising a thermoplastic polymer having a nitrogen permeability constant in the range 1×10^{-15} to 1×10^{-10} and being softenable upon heating above ambient temperature to permit the formation of light-scattering or reflecting gas vesicles therein, wherein at least one pigmented or dyed coating layer having an opacity represented by a total luminous transmittance measured by ASTM test method D-1003-61 not exceeding 25% is applied over the imaging layer and remote from the plastics sheet or film.

2. A material according to claim 1, wherein the vesicle-producing gas is released by a sensitising agent uniformly dispersed in the polymeric vehicle of the imaging layer upon exposure to light.

3. A material according to claim 1 or 2, in which the polymeric vehicle of the light-sensitive vesicular imaging layer comprises a polymer of vinylidene chloride.

4. A material according to claim 1, 2 or 3, in which the pigmented or dyed coating layer comprises from 5 to 30% by weight, based upon the weight of the polymeric vehicle, of a pigment or dye.

5. A material according to any preceding claim, in which the pigment included in the pigmented coating layer is selected from carbon black or the group consisting of Colour Index 74160, 15850, 69800, Pigment Yellow 34 and Azoic Blue 7.

6. A material according to any of claims 1 to 4, in which the dye included in the dyed coating layer is selected from the group consisting of Colour Index 12716,

12055, 61551, 60505, 47000, 50415, Solvent Blue 70, Solvent Red 60, Solvent Blue 49, Solvent Blue 53, Solvent Blue 67 and Solvent Blue 65.

7. A material according to any preceding claim, in which the pigmented or dyed coating layer comprises a polymeric binder having a nitrogen permeability constant greater than 1×10^{-15}.

8. A material according to claim 7, in which the polymeric binder is selected from the group consisting of nitrocellulose, cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, copolymers of vinyl chloride and vinyl acetate, copolymers of alkyl esters of methacrylic acid, styrene/acrylonitrile copolymers, and polyamides.

9. A material according to any preceding claim, in which a self-adhesive or pressure-sensitive adhesive layer is applied over the pigmented or dyed coating layer.

10. A material according to any preceding claim, in which a transparent pigmented or dyed layer is applied to the surface of the plastics sheet or film remote from the light-sensitive vesicular imaging layer.

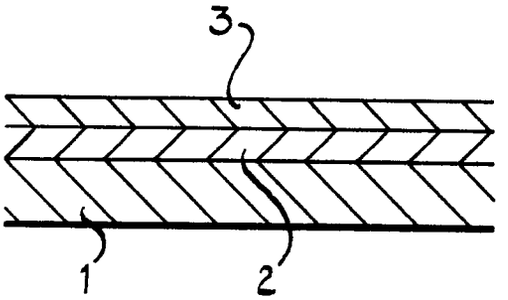

Fig. 1

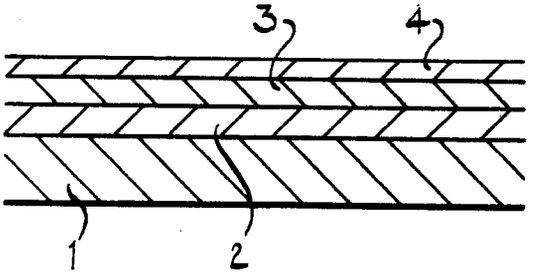

Fig. 2

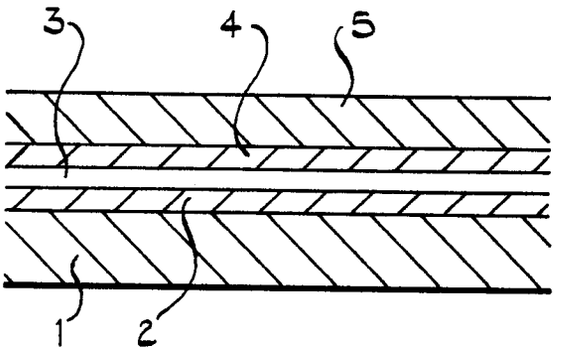

Fig. 3

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 78 0000 0084

0000425

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	FR - A - 933 955 (GAF) & GB - A - 645 825 * Page 2, lines 5-43; example 8 *	1,2,4-8, 10
D	GB - A - 1 276 608 (N.T. NOTLEY) * Claim 1 *	1,3
	US - A - 3 215 529 (R.M. LINDQUIST et al.) * Column 1, lines 42-65; column 3, lines 23-28 *	3
	FR - A - 2 098 849 (PITNEY-BOWES) * Claims 1,15 *	9
A	FR - A - 2 288 993 (KALVAR) * Page 15, line 37 to page 16, line 21; claim 1 *	1

CLASSIFICATION OF THE APPLICATION (Int. Cl.²)

G 03 C 5/00
G 09 F 3/00

TECHNICAL FIELDS SEARCHED (Int.Cl.²)

G 03 C 5/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	04-10-1978	PHILOSOPH