(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 395 170 A1

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 90201032.1

(22) Date of filing: 25.04.90

(51) Int. Cl.5: B41M 5/28

(30) Priority: 28.04.89 EP 89201106

(43) Date of publication of application: 31.10.90 Bulletin 90/44

(84) Designated Contracting States: DE

(71) Applicant: AKZO N.V.
Velperweg 76
NL-6824 BM Arnhem(NL)

(72) Inventor: Münch, Jürgen
Gartenstrasse 27
D-7123 Sachsenheim 1(DE)
Inventor: Metzger, Carl Walter
Mühlhaldenstrasse 56
D-7306 Denkendorf(DE)

(74) Representative: Schalkwijk, Pieter Cornelis et al
Akzo Patents Department P.O. Box 93 00
Velperweg 76
NL-6800 SB Arnhem(NL)

(54) **Method for developing a permanent image on an image layer including an optically anisotropic liquid crystalline material.**

(57) A method is provided for developing an essentially permanent and uniform image onto an image member including an optically anisotropic liquid crystalline material, wherein a degrading energy for the liquid crystalline material is selectively applied to a selected portion of the image member to at least partially degrade the liquid crystalline material in that selected portion, thereby altering the optical properties of the liquid crystalline material in that selected portion in comparison with the surrounding liquid crystalline material.

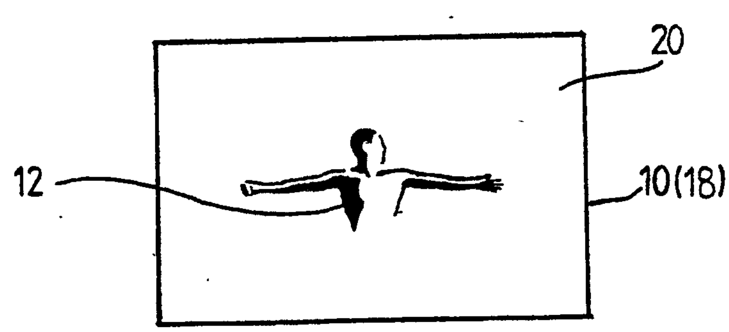

FIG. 2

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Method for Developing a Permanent Image on an Image Layer Including an Optically Anisotropic Liquid Crystalline Material

Background of the Invention

The present invention relates generally to imaging systems and, more particularly, to imaging systems in which an image is developed onto an image member including an optically anisotropic liquid crystalline material.

US3666947 and US3666948, both incorporated by reference herein for all purposes, disclose liquid crystal imaging systems in which an image is developed on an image member including an optically anisotropic liquid crystalline material. The image is developed by heating a selected portion of the image member to alter the texture state and, therefore, the optical properties of the liquid crystalline material therein. This alteration is reversible so that the images developed are not permanent but are erasable, allowing the image member to be reused as desired.

Optically anisotropic liquid crystalline materials have also been utilized in other reversible imaging systems such as, for example, temperature sensors. See, e.g., US3697297 and GB1249432, both of which are incorporated by reference herein for all purposes.

For many applications, particularly those of a decorative nature, a reusable image member wherein the image can be easily altered or erased is not desirable. For example, in the case where the image is a company logo to be placed on an article of manufacture for advertising purposes, an alteration of the image would destroy the usefulness of the article for its intended purpose.

US3969264, also incorporated by reference herein for all purposes, describes a method of reproducing a photograph by irradiating, through a negative, a film (image layer) including an optically anisotropic liquid crystalline material. Due to the deterioration of the liquid crystalline material through irradiation, it undergoes a change in temperature response characteristics. Such a method is said to produce an image which can be stable over long periods of time.

The use of standard liquid crystal coatings, in general, produces films having non-uniform appearance and effect characteristics. Images produced on such films, consequently, will also share these non-uniform characteristics, making consistent and reproducible results at best extremely difficult.

The present invention, however, provides an imaging system including an optically anisotropic liquid crystalline material and method for producing an image in conjunction therewith but, in contrast to the systems and methods of the above references, the image so formed is not only essentially permanent but also quite uniform and reproducible.

Summary of the Invention

In its overall concept, the present invention provides a method for developing an image onto an image member, the image member comprising an image layer applied over a suitable substrate, and the image layer comprising a thin film including an optically anisotropic liquid crystalline material and having at least a first and second selected area, wherein a degrading energy for the optically anisotropic liquid crystalline material is selectively applied to the first selected area of the image layer to at least partially degrade the liquid crystalline material therein, thereby permanently altering an optical property of the liquid crystalline material in the first selected area in contrast to that of the liquid crystalline material in the second selected area, characterized in that the thin film of the image layer is produced from a composition selected from:

(1) a composition comprising an aqueous dispersion binder component, a flop effect pigment and an encapsulated thermochromic liquid crystalline material; and

(2) a composition including a liquid crystal pigment comprising a laminar particle at least partially coated with a liquid crystalline material.

It is preferred that the image layer should comprise a thin coating film produced fro a coating composition selected from the type as just described.

JP 74020967, also incorporated by reference, discloses what on first glance appears to be a similar permanent imaging system; however, the system of this reference again operates in a totally different manner. This reference teaches to utilize the liquid crystalline material incorporated in a microcapsule with a photosensitive silver halide shell, which shell turns black upon exposure to light. The remaining silver halide from the unexposed microcapsules is removed by development, leaving the liquid crystalline material in the unexposed portion. The system of this reference, therefore, is completely distinguishable from that of the present invention since the liquid crystalline material itself is not exposed to the degrading energy and, consequently, not degraded.

By the method of the present invention, the optical properties of the liquid crystalline material in the first selected area of the image member are altered in contrast to those of the second and other selected areas, which may be undegraded, degraded to a different extent or even totally degraded. The resulting contrast in the optical properties of the various selected areas of the image member is the basis for the image formation.

The first selected area can be, for example, the area of the image member on which the image is to be developed, or the area of the image member which is to be the background for the image. The second selected area can be, for example, the other of the image or background areas. Additionally, as indicated above, more than one selected area can be exposed, each to varying amounts of degrading energy, to thereby produce varying liquid crystal effects at a number of different selected areas of the image member. This allows for the developement of more complex images on the imaging layer.

Due to the use of the particular compositions as generally set forth above and further described below, the images so formed are not only essentially permanent but also quite uniform and reproducible.

Once the image is developed, the liquid crystalline material in the image member should be protected from substantial further degradation by, for example, coating the image member with a protective layer containing a UV absorber.

The liquid crystal images so produced are suitable for a variety of purposes, primarily of a decorative nature.

These and other features and advantages of the present invention will be more readily understood by those skilled in the art from a reading of the following detailed description with reference to the accompanying drawings.

Brief Description of the Drawings

FIG. 1 is a schematic, in partial cross-section, illustrating an image member having an image being developed thereon in accordance with one embodiment of the present invention.

FIG. 2 illustrates, in one aspect, an overhead view of a stencil member which may be used for developing an image on the image member and, in another aspect, an overhead view of an image member with an image developed and visible thereon.

Detailed Description of the Preferred Embodiments

Referring now to the drawings in more detail, and particularly to FIG. 1, there is depicted a schematic of an image member 10 having an image 12 (FIG. 2) being developed thereon in accordance with one embodiment of the present invention.

Image member 10 comprises an imaging layer 10a, which includes a liquid crystalline material, applied over a suitable substrate 10b for support. Imaging layer 10a may take the form of thin film, for example, a thin coating film, laminate, sheet or the like, which comprises at least the desired type or types of liquid crystalline material. In preferred embodiments, as discussed below, imaging layer 10a comprises a thin coating film produced from a coating composition including the liquid crystalline material in microencapsulated and/or laminar form.

The thickness of imaging layer 10a may vary widely, but should be thin enough so that the liquid crystals at a selected portion can be substantially evenly degraded throughout by exposure to a degrading energy for the liquid crystals, as further described below. Preferred thicknesses for image layer 10a generally range from about 1 μm to about 50 μm, more preferably from about 5 μm to about 25 μm.

Liquid crystals, as is well-known, include a large number of compounds which, in a liquid state, display properties typically observed in crystalline solids. Liquid crystalline materials suitable for use with the present invention are, as indicated before, those that display optical anisotropies, for example, those which undergo an appearance change in response to an external stimulus. Preferred are those liquid crystalline materials which undergo a color change in response to an external stimulus such as, for example, a temperature change.

This particular class of liquid crystalline material is well-known to those skilled in the art and includes, for example, various chiral nematic cholesterol and biphenyl derivatives. For further details about this type of liquid crystalline material, reference may be had to the following literature which is incorporated by reference herein for all purposes: H. Finkelmann and G. Rehage, "Investigation on Liquid Crystal Polysiloxanes, 1 - Synthesis and Characterization of Linear Polymers," Makromol. Chem., Rapid Commun., 1 (1980), pp.31-34; G. Rehage, "Flüssigkristalline Polymere," Nachr. Chem. Tech. Lab., 32, No. 4 (1984), pp.287-95; "Flüssigkristalle," Ullmanns Encyklopädie der Technischen Chemie (1976).

Most preferred of these liquid crystalline materials are those formed from precursors comprising a polysiloxane backbone with suitable mesogenic sidechains like, for example, various cholesterol and biphenyl derivatives. Such liquid crystalline materials are well-known in the art, as exemplified by the above-incorporated literature, and reference may be had to such for further details.

The particular type of liquid crystalline material chosen must be degradable by exposure to a degrading energy source, most preferably ultraviolet radiation and/or thermal energy. The particular type of degrading energy for a particular type of liquid crystalline material is well-known, and such information is readily available, to those skilled in the art.

The liquid crystalline material may be incorporated into imaging layer 10a in any well-known fashion. In the preferred embodiment, better and more uniform effects are obtained by incorporating the liquid crystals in microencapsulted form in combination with a flop effect pigment, or in laminar form as a laminar particle at least partially coated with a liquid crystalline material, optionally dispersed within an suitable binder composition, such as described in EP-A-0357844 (European Patent Application No. 88201966.4) and European Patent Application No. 90200266.6 (claiming priority from European Patent Application No. 89200324.5), both of which are hereby incorporated by reference for all purposes.

More specifically, EP-A-0357844 teaches a thermochromic effect coating comprising an aqueous dispersion binder component, a flop effect pigment and a microencapsulted liquid crystal pigment. As preferred aqueous dispersion binder components may be mentioned acrylic and/or polyurethane dispersion resins, especially those suited for metallic effect coatings. As preferred flop effect pigments may be mentioned those selected from various aluminum and mica pigments which are or can be made substantially stable in aqueous systems. The microencapsulted liquid crystal pigment comprises a liquid crystalline material, of the type described above, which has been microencapsulated in any well-known fashion.

European Patent Application No. 90200266.6 teaches a coating including the liquid crystalline material in the form of a laminar particle, more specifically a laminar particle at least partially coated with a liquid crystalline material. The coating procedure is preferably accomplished by the steps of (a) dissloving a liquid crystalline material in a suitable solvent, (b) dispersing a laminar particle in the solvent and (c) at least partially coating the laminar particle by precipitating at least a portion of the liquid crystalline material from the solution onto the laminar particle. It should be noted that the order of performing steps (a) and (b) is not important. The resulting liquid crystal solution, with the liquid crystal pigment dispersed therein, may be used directly or in modified form as the coating, or the liquid crystal pigment may be recovered from solution and utilized later, for example, dispersed in a suitable binder in the fashion of a normal pigment.

Reference may be had to EP-A-0357844 and European Patent Application No. 90200266.6 for further details.

The liquid crystalline material can also be incorporated into thermoplastic and similar laminates and sheets in like well-known manners.

Substrate 10b may comprise any suitable material such as, for example, metal, wood or plastic, as long as the material chosen is compatible with the other components of imaging layer 10a. The substrate may be transparent, translucent or opaque, but it is preferred that at least the surface of substrate 10b in contact with imaging layer 10a be dark or darkened, preferably black, to obtain the maximum visual effect when the preferred liquid crystals (color variant) are utilized. As an example of an especially preferred substrate may be mentioned a mat type of plastic foil such as currently used in the car refinish area for the repair of relatively small areas of topcoat damage. Such a system is typified by one commercially available under the trade designation Transcolor from Kurt Vogelsang GmbH.

Referring again to FIG. 1, the image 12 (FIG. 2) is developed on imaging layer 10a by the selective application of a degrading energy, shown generally as 14, to one or more selected areas of imaging layer 10a. As shown in FIG. 1, the degrading energy can be, for example, ultraviolet light and/or heat from a source 16 (such as a lamp) selectively applied to imaging layer 10a through the use of a stencil member 18.

As depicted in FIG. 2, stencil member 18 comprises a transparent sheet 20 with an opaque and/or reflective image 12 applied thereto. Of course, stencil member 18 can comprise an opaque sheet 20 with a transparent image 12, or can take any number of other well-known forms such as as die cut sheets, formed images and the like, generally anything capable of forming a positive or negative image on imaging layer 10a.

As shown in Fig. 1, as the degrading energy 14 is applied to imaging layer 10a, the liquid crystalline material therein is at least partially degraded except at the particular area covered by image 12 of stencil member 18, which reflects or otherwise fully or partially screens the degrading energy (the screened degrading energy is shown as 14a) from image layer 10a. Stencil member 18 should be placed close to, preferably substantially on top of, imaging layer 10a to prevent scattering of the degrading energy into other selected portions of imaging layer 10a which are, for example, to remain unexposed.

As alternatives to the use of stencil member 18 and source 16 as depicted in FIG. 1 may be mentioned, for example, lasers, light pens or like devices which can be utilized to draw images onto imaging layer 10a. The use of a system such as depicted in FIG. 1 can, in many instances, provide a more uniform effect, while the options mentioned above can, in many instances, provide better image details. Combinations of these various systems may also be utilized to obtain the advantages of each.

By at least partially degrading the liquid crystalline material in one or more selected areas of imaging layer 10a, the optical properties of the liquid crystalline material in those selected areas are permanently altered. The liquid crystalline material can be "totally" degraded, whereby no optical effect remains, "partially" degraded, whereby the optical effect is altered, or remain substantially undegraded. The result is that, under conditions in which the liquid crystalline material displays its optical properties, the optical effect will be different for the undegraded selected areas as compared with the "partially" degraded selected areas, with no optical effect from the "totally" degraded selected areas. An image 12, therefore, will become visible.

As mentioned earlier, the first selected area can be, for example, the area of the image member on which the image is to be developed (positive), or the area in the image member which is to be the background of the image (negative), while the second selected area can be, for example, the other of the image or background areas. Additionally, more than one selected area can be exposed, each to varying amounts of degrading energy, to thereby produce varying liquid crystal effects at a number of different selected areas of the image member. This allows for the developement of complex images on the imaging layer.

Because the liquid crystalline material will be at least partially degraded, the change in the optical properties is irreversible. Image 12, therefore, becomes essentially permanent and fixed other than through further degradation of the liquid crystalline material.

Once image 12 has been developed into imaging layer 10a, a protective layer, such as a clear topcoat containing a UV absorber, should be applied over imaging layer 10a to protect against physical damage and further degradation of the liquid crystalline material to maintain the image developed thereon. Any number of topcoats utilizable in the coatings industry should be suitable as long as the components of the topcoat are compatible with the other components of image member 10. A number of suitable topcoats are mentioned in the aforementioned incorporated EP-A-0357844 and European Patent Application No. 90200266.6.

The foregoing more general discussion of the invention will be further exemplified by the following specific examples offered by way of illustrationand not limitation of the above-described invention.

Example 1

An image member was formed by spraying a thermochromic effect coating, as detailed in Example 1 of EP-A-0357844, to a layer thickness of 15-20µm onto a Bonder 132 steel panel, which had been precoated with a black primer (commercially available under the trade designation Primer Black 03-59622 from Akzo Coatings GmbH). The thermochromic effect coating was subsequently dried for 10 minutes at 60 °C.

A stencil was prepared by photocopying an image (12 of Fig. 2) onto a transparent plastic foil ("Tageslicht Transparent für Normalpapierkopieren, Type 688" commercially available from the 3M Company). The resulting stencil was laid onto the image member and the whole illuminated for 12 hours with a 500W UV-lamp (commercially available under the trade designation Type Q700 from Hanau GmbH). The distance between the lamp and the stencil was about 10 cm.

After illumination, the thermochromic effect coating was overcoated with a 2-component solvent-based clearcoat (commercially available under the trade designation Autocryl MS from Akzo Coatings GmbH) by spraying to a layer thickness of 40-45µm, which was predried for 30 minutes at 60 °C then subsequently dried for 7 days at room temperature.

The resulting image member had a black metallic appearance at room temperature. On warming the panel, the exposed portion (background) began exhibiting typical thermochromic color changes, while the unexposed area (image) remained black. A sharp picture of the image was thereby formed. As the panel was further warmed, the background again became black while the image began to exhibit the typical thermochromic color changes. The same sharp picture of the image was again formed, but in reverse.

Example 2

Example 1 was repeated, except that a reverse image was formed on the stencil wherein the image was clear and the background opaque.

As with Example 1, the resulting image member had a black metallic appearance at room temperature. On warming the panel, the exposed portion (image) began exhibiting typical thermochromic color changes, while the unexposed area (background) remained black. A sharp picture of the image was thereby formed.

As the panel was further warmed, the image became black while the background began to exhibit the typical thermochromic color changes. The same sharp picture of the image was again formed in reverse.

Example 3

Example 1 was repeated, except that illumination was carried out using a UV-drying plant commercially available as Serial No. 403 from Wallace Knight Ltd., Slough, England. The plant had a rating of 120 watts/cm^2 and a conveyor speed through the plant of 150 cm/min. The UV lamp was 8-9 cm above the image member, with the stencil being a brass cut-out profile of the image of Fig. 2.

Again, the resulting image member had a black metallic appearace at room temperature. Upon warming, the area covered by the brass cut-out (image) began to exhibit the typical thermochromic effect, while the exposed portion (background) remained black. A sharp picture of the image was thereby formed.

Example 4

An image member was formed by the procedure as set forth in Example 2 of European Patent Application No. 90200266.6. Prior to application of the clearcoat, the image member was illuminated as set forth in Example 3, and a clearcoat layer applied and dried as in Example 1.

The resulting image member exhibited the image in the unexposed area, while the background (exposed area) remained black (total degradation-no liquid crystal effect remaining).

Many modifications and variations can be made to the embodiments specifically mentioned here without departing substantially from the concept of the present invention. Accordingly, it should be clearly understood that the preferred form of the invention described herein is exemplary only, and is not intended as a limitation on the scope thereof.

Claims

1. A method for developing an image onto an image member, the image member comprising an image layer applied over a suitable substrate, and the image layer comprising a thin film including an optically anisotropic liquid crystalline material and having at least a first and second selected area, wherein a degrading energy for the optically anisotropic liquid crystalline material is selectively applied to the first selected area of the image layer to at least partially degrade the liquid crystalline material therein, thereby permanently altering an optical property of the liquid crystalline material in the first selected area in contrast to that of the liquid crystalline material in the second selected area, characterized in that the thin film of the image layer is produced from a composition selected from:

(1) a composition comprising an aqueous dispersion binder component, a flop effect pigment and an encapsulated thermochromic liquid crystalline material; and

(2) a composition including a liquid crystal pigment comprising a laminar particle at least partially coated with a liquid crystalline material.

2. The method according to claim 1, characterized in that the image layer comprises a thin coating film produced from a coating composition selected from:

(1) a coating comprising an aqueous dispersion binder component, a flop effect pigment and an encapsulated thermochromic liquid crystalline material; and

(2) a coating including a liquid crystal pigment comprising a laminar particle at least partially coated with a liquid crystalline material.

3. The method according to claim 1, characterized in that the image layer comprises a thickness in the range of from about 1μm to about 50μm.

4. The method according to claim 1, characterized in that, after the image is developed, a protective layer is applied over the image member.

5. The method according to claim 1, characterized in that the degrading energy is UV radiation.

6. The method according to claim 1, characterized in that the optically anisotropic liquid crystalline material undergoes a color change in response to an external stimulus.

7. The method according to claim 1, characterized in that the aqueous dispersion binder component of composition (1) comprises an acrylic and/or polyurethane based aqueous dispersion resin.

8. The method according to claim 1, characterized in that the flop effect pigment is selected from aluminum and mica pigments.

9. The method according to claim 1, characterized in that the laminar particle comprises a laminar pigment.

10. The method according to claim 1, characterized in that the laminar particle comprises an average particle diameter of from about 5μm to about 500μm.

11. An image member comprising an image developed thereon in accordance with the method of any one of claims 1-10.

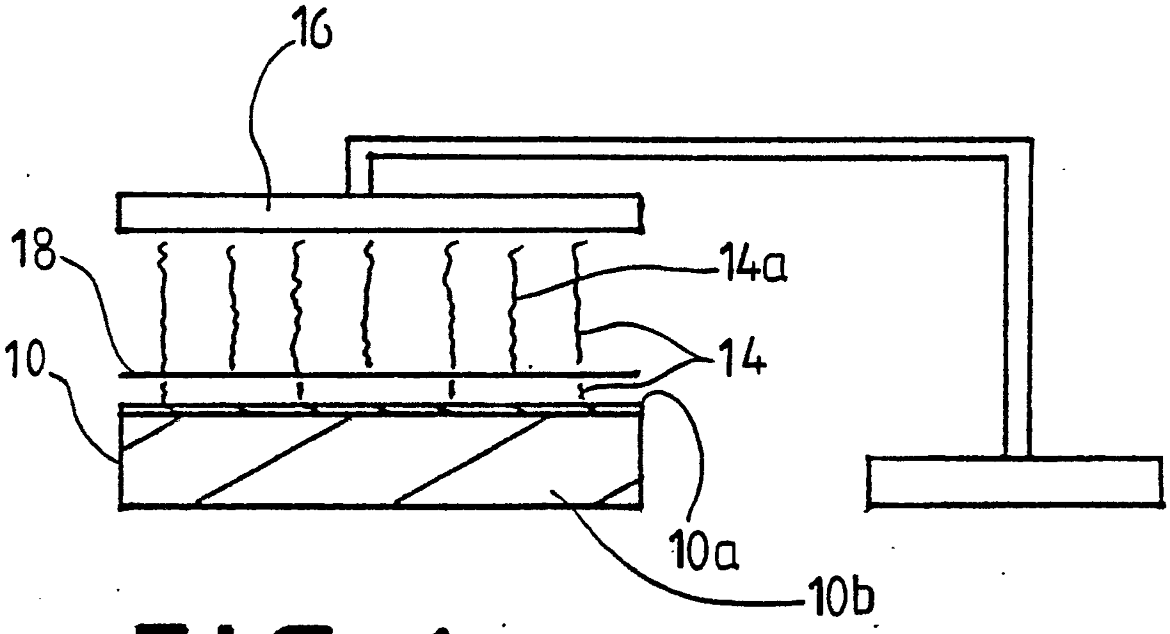

FIG. 1

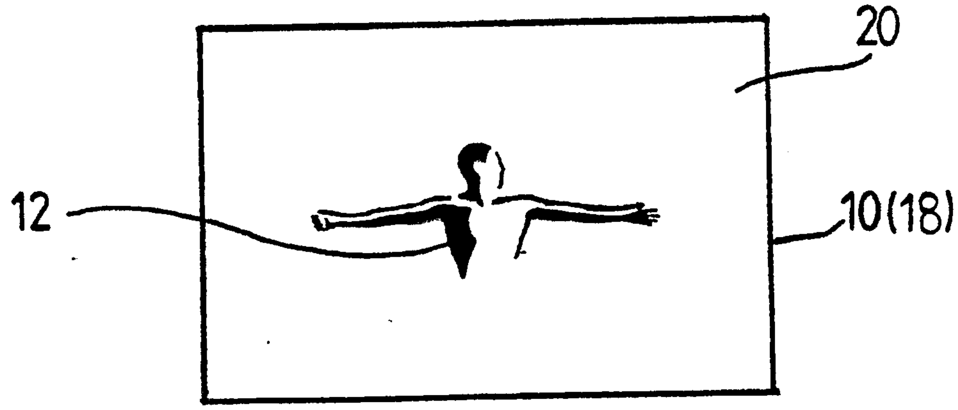

FIG. 2

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 20 1032

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	J. ELECTROCHEM. SOC.: SOLID-STATE SCIENCE AND TECHNOLOGY, vol. 121, no. 12, December 1974, pages 1667-1669; W.E. HAAS et al.: "U.V. imaging with nematic chlorostilbenes" * The whole document * -----	1	B 41 M 5/28
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B 41 M 5/00 G 02 F 1/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07-08-1990	DIOT P.M.L.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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