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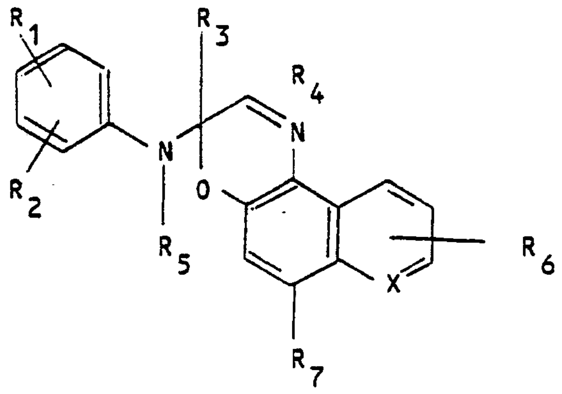
⑤④ Photochromatic composition and photochromatic articles which contain it.

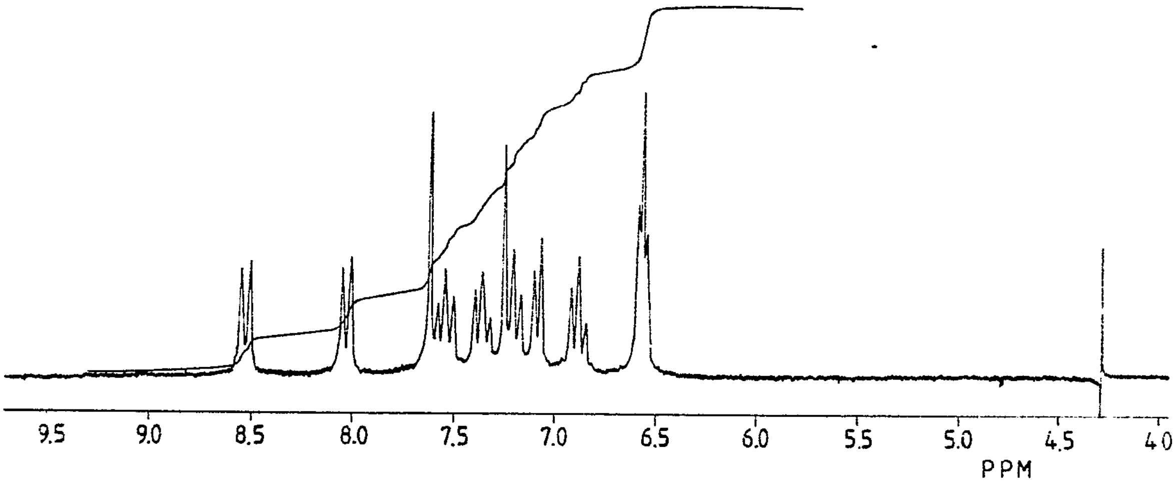
⑤⑦ A photochromatic composition contains at least two photochromatic compounds, defined by the general formula:



wherein the various substituents from R_1 to R_7 and X are as defined in the specification.

In such a mixture, at least one photochromatic compound is defined by the general formula, wherein R_7 represents a hydrogen atom, and at least one further compound is also defined by the general formula, wherein R_7 represents an $-NR_8\ R_9$, with R_8 and R_9 having the meaning as defined in the text.

Fig.1



PHOTOCHROMATIC COMPOSITION AND PHOTOCHROMATIC ARTICLES WHICH CONTAIN IT

The present invention relates to a photochromatic composition which contains at least two organic photochromatic compounds.

The photochromatic compounds are substances which display the characteristics of reversibly changing in colour and/or degree of light transmission when they are exposed to some types of electromagnetic radiation, and to sun light, turning back into their original colour and transmission status when the initial light source is removed.

The substances endowed with photochromatic characteristics known from the prior art are many, and belong to several classes of both inorganic and organic compounds, as described, e.g., in "Photochromism", G.H. Brown (Ed.), Vol. IV, from the Weisseberger Series "Techniques of Organic Chemistry", Wiley-Interscience, New York (1971).

Among the organic photochromatic compounds, in particular those belonging to the class of the spiro-indolino-naphtho-oxazines are known, which are capable of conferring photochromatic characteristics on polymerized and transparent organic materials (organic glasses), for their use as sun filters and photochromatic optical articles, such as disclosed, e.g., in the following patents: US 3,562,172; US 3,578,602; US 4,215,010; US 4,342,668; EP 146 135, WO 85/02619; EP 245 020; and in European patent applications publ. Nos. 134,633 and 141,407.

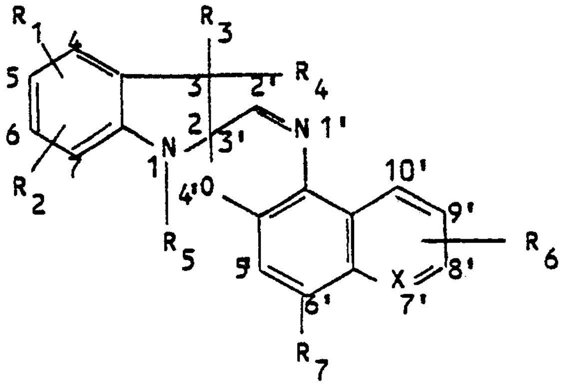
The known photochromatic compounds belonging to the class of the spiro-indolino-naphtho-oxazines exhibit, as compared to other known organic photochromatic compounds (e.g., those belonging to the class of the spiro-piranes) the advantage of having a much higher fatigue strength, when they are submitted to repeated cycles of colouring and de-colouring; and a much higher ageing resistance when they are exposed to sun light, or to artificial ageing tests. This behaviour is very advantageous for the above set out uses.

However, the organic photochromatic compounds known from the prior art are practically colourless in their deactivated status, both in solution in common organic solvents, as well as when they are incorporated in transparent polymeric materials, and turn to a generally blue colour when they are activated. This blue colour is a disadvantage for their use as optical photochromatic articles, in particular in the ophthalmic sector, for which more neutral colours please, e.g., the gray colour.

Furthermore, the photochromatic effect obtained is in many cases of low intensity as regards the change in transmittance in the visible wavelength range. In other cases, such a change, although is satisfactory at low temperatures, is depressed down to unacceptedly low values with increasing temperature, even if within the values as required in practical use. Finally, the activation of the spiro-indolino-naphtho-oxazines, obtained under controlled laboratory conditions by irradiation with UV light of several wavelengths from about 320 to about 380 nm, is often not reproduced with the same satisfactory intensity when the exposure is carried out to the spectrum of frequencies and of relative intensities of sun light, as required for the ophthalmic use, and as sun filter.

The purpose of the present invention is overcoming the drawbacks which affect the prior art by means of a novel photochromatic composition containing at least two photochromatic compounds belonging to the class of the spiro-indolino-naphtho-oxazines.

In accordance therewith, the present invention relates to a photochromatic composition consisting of at least two photochromatic compounds, both of which can be represented by the following general formula (I):



(I)

wherein:

R_1 and R_2 independently represent a hydrogen atom or a halogen atom (chlorine, bromine or fluorine), or a group selected from: $(C_1$-$C_5)$-alkoxy; nitro; cyano; and a linear or branched $(C_1$-$C_5)$-alkyl either unsubstituted or substituted with one or more halogen (chlorine, bromine and fluorine) atoms, or $(C_1$-$C_5)$-alkoxy, $(C_1$-$C_5)$-alkyl-thio, $(C_1$-$C_5)$-carboxy-alkyl and cyano groups; or

R_1 and R_2, when are not hydrogen, can be linked to any of the 4-, 5-, 6- and 7-positions of the indolinic moiety;

R_3 and R_4 independently represent linear or branched $(C_1$-$C_5)$-alkyl group, phenyl or benzyl; or

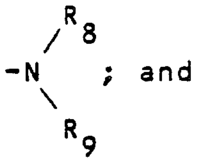
R_3 and R_4, when considered jointly together with the carbon atom to which they are linked, form a $(C_1$-$C_8)$-cycloalkyl group;

R_5 is a phenyl; benzyl; allyl group; or a linear or branched $(C_1$-$C_5)$-alkyl group, either unsubstituted or substituted with one or more halogen (chlorine, bromine and fluorine) atoms, or $(C_1$-$C_5)$-alkoxy, $(C_1$-$C_5)$-alkyl-thio, $(C_1$-$C_5)$-carboxy-alkyl and cyano groups;

R_6 represents a hydrogen atom, a halogen (chlorine, bromine or fluorine) atom, or a group selected from $(C_1$-$C_5)$-alkoxy, $(C_1$-$C_5)$-alkyl-thio, $(C_1$-$C_5)$-carboxy-alkyl and cyano groups; and a linear or branched $(C_1$-$C_5)$-alkyl group, either unsubstituted or substituted with one or more halogen (chlorine, bromine and fluorine) atoms, or $(C_1$-$C_5)$-alkoxy, $(C_1$-$C_5)$-alkyl-thio, $(C_1$-$C_5)$-carboxy-alkyl and cyano groups; or represents a condensed aromatic or heterocyclic ring;

R_6, when it does not represent hydrogen, or a condensed aromatic or heteocyclic ring, can be in any one of the 7'-, 8'-, 9'-, 10'-positions of the naphthenic moiety;

R_7 represents either a hydrogen atom, or an



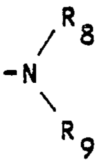
$-N\begin{matrix}\diagup R_8\\ \diagdown R_9\end{matrix}$; and

R_8 and R_9 represent, independently from each other, a hydrogen atom, or a linear or branched $(C_1$-$C_5)$-alkyl group, phenyl or benzyl; or

R_8 and R_9, when considered jointly together with the nitrogen atom to which they are linked, form a mono-cyclic or poly-cyclic structure, of from 5 to 12 members, possibly containing a further heteroatom selected from between oxygen and nitrogen; and

X represents either -CH- or N;

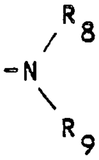
in which composition at least one of the photochromatic compounds having formula (I) is characterized in that it has the R_7 substituent constituted by hydrogen, and at least one of the photochromatic compounds having formula (I) is characterized in that it has the R_7 substituent constituted by a group



$-N\begin{matrix}\diagup R_8\\ \diagdown R_9\end{matrix}$

wherein R_8 and R_9 have the above seen meanings.

In the preferred form of practical embodiment, the photochromatic compounds of the composition according to the present invention, all of which can be defined by means of the general formula (I), and with the proviso that in at least one of them the R_7 substituent represents a hydrogen atom and in at least one of them the R_7 substituent represents the amino group



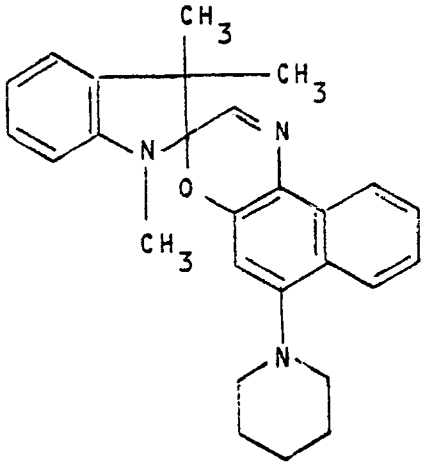
$-N\begin{matrix}\diagup R_8\\ \diagdown R_9\end{matrix}$

the R_1, R_2, R_3, R_4, R_5, R_6, R_7, and, if present, R_8 and R_9, substituents, have the following meaning:
R_1 and R_2 independently represent the hydrogen atom, or the methyl, methoxy or halogen groups;
R_3 and R_4 represent each the methyl or ethyl group, or, when considered jointly, represent the cyclohexyl group;
R_5 represents a (C_1-C_5)-alkyl group;
R_6 represents the hydrogen atom or the methoxy group;
R_8 and R_9 jointly represent, together with the nitrogen atom to which they are linked, the piperidino, morpholino, pyrrolidinyl or hexamethylene-imino group; and
X represents either -CH- or N.

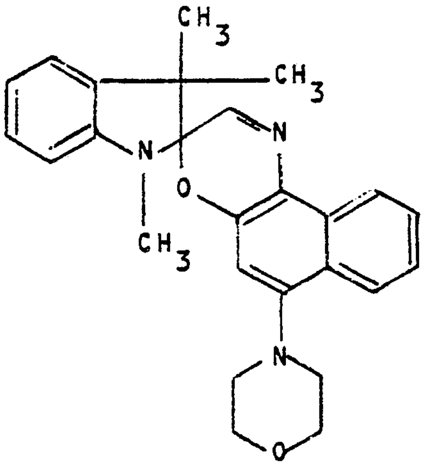
Furthermore, still in the preferred form of practical embodiment, the R_1, R_2 and R_6 groups, when they do not represent hydrogen, or, in case of R_6 group, a ring structure, are respectively linked to the (4,5)- or (5,6)- and 9′-positions of the molecule.

Specific examples of photochromatic compounds in which the R_7 substituent is different from hydrogen, are:

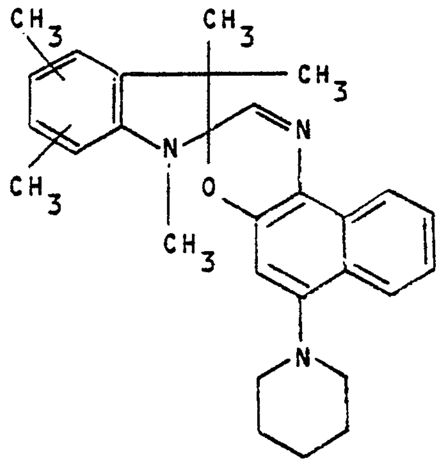
A) 1,3,3-Trimethyl-6′-piperidino-spiro-[indolino-2,3-(3H)-naphtho-(2,1-b)-(1,4)-oxazine].



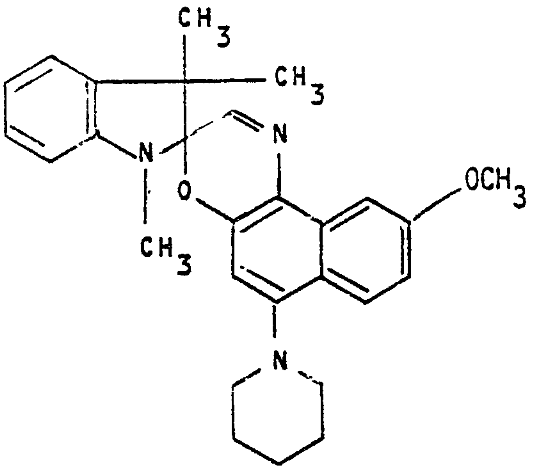
B) 1,3,3-trimethyl-6′-morpholino-spiro[indolino-2,3-(3H)-naphtho-(2,1-b)-(1,4)-oxazine].



C) 1,3,3,4,5,-(or 1,3,3,5,6)-pentamethyl-6′-piperidino-spiro-[indolino-2,3′-(3H)-naphtho-(2,1-b)-(1,4)-oxazine].

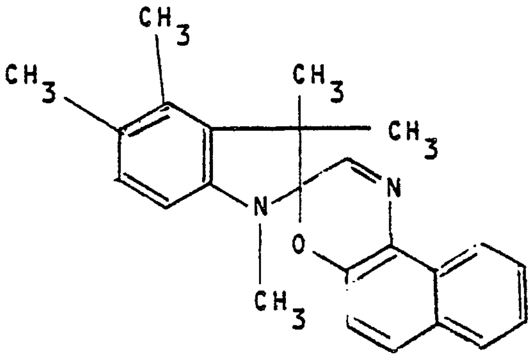


D) 1,3,3-trimethyl-6′-piperidino-9′-methoxy-spiro-[indolino-2,3′-(3H)-naphtho-(2,1-b)-(1,4)-oxazine].

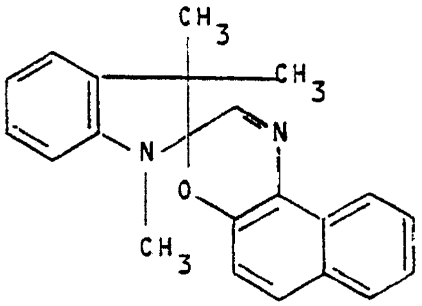


Specific examples of photochromatic compounds in which the R_7 substituent is hydrogen are:

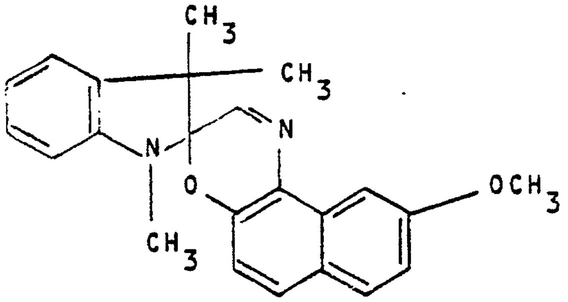
E) 1,3,3,4,5- (or 1,3,3,5,6) pentamethyl-spiro-[indolino-2,3′-(3H)-naphtho-(2,1-b)-(1,4)-oxazine].



F) 1,3,3-trimethyl-spiro-[indolino-2,3′-(3H)-naphtho-(2,1-b)-(1,4)-oxazine] .



G) 1,3,3-trimethyl-9′-methoxy-spiro-[indolino-2,3′-(3H)-naphtho-(2,1-b)-(1,4)-oxazine].



The above listed photochromatic compounds have been incorporated into transparent organic polymers by means of techniques depending on the polymer used.

In the photochromatic mixture of the present invention, the simultaneous presence of a photochromatic compound definable by means of formula (I) and having an -NR_8 R_9 in the 6′-position of the molecule, and of a photochromatic compound definable by means of said formula, but in which the substituent in 6′-position is hydrogen atom, is advantageous.

In such a mixture, as said, both compounds act with a synergistic effect on the regulation of the sun light, generating a more intense colour, and with shorter response times, than the normal photochromatic organic compounds of the prior art, as well as than the individual components of the same mixture.

The change in transmittance is furthermore maintained at satisfactory values with increasing room temperature, and much higher than as required by the practical application. Furthermore, the shades of colour which can be obtained by means of the use of the photochromatic mixture of the present invention are more neutral than the blue colour generally shown by individual components, and can be modulated within a wide range by means of a properly balanced dosage of both basic components, as well as of other components known from the prior art.

Advantageously, this mutual mol ratio of the two photochromatic components defined by the general formula (I) and respectively bearing the -NR_8 R_9 group and hydrogen in the 6′-position, is a number comprised within the range of from 0.1 and 9 and preferably from 0.2 to 1.5.

As said, the photochromatic mixture of the present invention can be constituted by more than two compounds as defined by the general formula (I), provided that at least two of them are different from each other as to the 6′-substituent, as above said.

Said mixtures can furthermore additionally contain other components, such as the U.V. stabilizers known from the prior art, capable of improving the duration of the photochromatic effect, without impairing the intensity of photocolourability of the same mixtures. Non-limitative examples of U.V.-stabilizers for the purposes of the present invention are the hindered ammines (HALS).

The photochromatic mixture according to the present invention is useful in the production of photochromatic articles endowed with particular colour transitions, a high activation by exposure to sun light, a high fatigue and ageing resistance.

The photochromatic mixture according to the present invention is applied to the surface of, or is incorporated into, the desired articles, generally constituted by transparent polymeric materials, by means of suitable techniques. Photochromatic polymeric articles can be obtained by means of moulding techniques (e.g., injection-moulding, press-moulding, and so forth;) by homogeneously dispersing throughout the mass the photochromatic mixture.

According to an alternative route, the mixture can be dissolved in a suitable solvent, together with a polymeric material (e.g., poly-methyl-methacrylate, polyvinyl-alcohol, poly-vinyl-butyral, cellulose acetate-butyrate or epoxy resin, polysiloxane resin or urethane resin, and so forth), and deposited on a transparent support in order to form, after the evaporation of the solvent, a photochromatic coating.

According to an alternative route, the photochromatic mixture can be added to a polymerizable monomer, e.g., methyl-methacrylate, so that after a polymerization carried out in the presence of a suitable polymerization initiator, e.g., azo-bis(isobutyronitrile), it results to be evenly incorporated to the formed resin.

According to an alternative route, the photochromatic mixture can be dissolved in a suitable solvent, in the presence of a resin, as above disclosed, and from this solution, by evaporating the solvent, a photochromatic film or sheet can be formed, which contain the uniformly dispersed photochromatic mixture.

According to an alternative route, the photochromatic mixture can be applied to a transparent substrate (e.g., a polycarbonate substrate, a polymethyl-methacrylate substrate or a poly-diethylene-glycol-bis(allyl carbonate) substrate) by means of a surface impregnation obtained by placing the substrate into contact, at a suitable temperature, with a solution or dispersion which contains the mixture.

In particular, by means of the above disclosed techniques, photochromatic articles can be obtained, such as photochromatic ophthalmic lenses and photochromatic sun filters, that is to say, which are capable of constituting an at least partial screen towards the sun radiation, in a reversible way.

Such articles can be advantageously used, e.g., as lenses for sun glasses, prescription-lenses, contact lenses, glasses for cars or transport means in general, and windows in the building sector.

The following experimental examples are reported in order to illustrate the present invention without limiting it. The compounds reported in the Examples were prepared according to methods known from the prior art.

In particular, optical photochromatic articles of polymethyl-methacrylate (PMMA) were obtained by adding the photochromatic compound and the polymerization initiator azo-bis(isobutyro-nitrile) (AIBN) to the monomer and then carrying out the polymerization by casting into moulds of a suitable shape.

Optical articles of poly-diethylene-glycol-bis(allyl-carbonate) were made photochromatic by means of a surface impregnation technique. For that purpose, a solution or suspension is prepared of the photochromatic compound in a suitable solvent or dispersant, normally selected from among the usual organic solvents, silicone oils, fluorinated oils, and the like, and the photochromatic compound is transferred on to the polymeric substrate by dipping the polymeric article in said solution or suspension, for suitable times and at suitable temperatures.

A more detailed disclosure of the application processes used is given in the hereinunder reported experimental examples.

On the optical photochromatic articles obtained, the following characteristics are determined:

-The U.V.-visible spectrum in the deactivated status (optical density at λ_{max}), as determined by the Cary 2300 spectrophotometer.

- The change in light transmittance (Δ Y) at 23° C, as determined by the MACBETH spectrophotometer, after a 120-second activation with an UV-A lamp of 9 W/m^2 of irradiance. The values of Δ Y were also measured after a 4-minute exposure to sun light, by using the Gardner's Hazemeter XL 211.
- Kinetics of return to the deactivated form (time for recovery of 50% of the initial transmittance, $t_{1/2}$), by means of a MACBETH spectrophotometer, under the same activation conditions as hereinabove disclosed.
- Ageing resistance, as determined by means of an Atlas Weather-0-Meter equipped with a continous-irradiation xenon lamp of 6,500 W, operating at a temperature of 63° C on the reference black panel, and at a relative humidity of 50%. The ageing resistance is evaluated by measuring, after various times of exposure in the Weather-0-Meter, the values of optical density at λ_{max} of the deactivated form, and the residual value of Δ Y after activation with the UV-A lamp.

Example 1

Photochromatic lenses of poly-diethylene-glycol-bis(allyl-carbonate) are prepared by means of surface impregnation with mixtures of (A) and (E) photochromatic compounds in the following proportions:

Photochromatic Mixture	(a)	(b)	(c)
(A) Compound (% by weight)	20	30	40
(E) Compound (% by weight)	80	70	60

In particular, a dispersion of 2% by weight of said (a), (b) or (c) mixture in silicone oil is prepared.

In order to transfer the photochromatic compound, the lens is dipped into the siliconic dispersion for times ranging from 30 to 90 minutes, and at temperatures comprised within the range of from 170 to 190 °C, as a function of the desired value for optical density. At the end of the impregnation, the lens is washed with petroleum ester, and the characteristics as listed hereinabove in the specification are evaluated.

The results relevant to the (a), (b) and (c) photochromatic mixtures are reported in Table (I), as compared to those obtained on a lens obtained, under the same conditions, by using the (A) photochromatic compound alone.

Table 1

Photochromatic Compound/ Composition	Optical Density (λ_{max})	Optical Status Colour	ΔY (23°C)	$t_{1/2}$ (23°C sec.)
(a) Composition	3,807 (348 nm)	gray-blue	32.2	44
(b) Composition	3,699 (350 nm)	gray-blue	36.1	50
(c) Composition	4,116 (350 nm)	gray-violet	34.9	45
(A) Photochromatic Compound	2,796 (362 nm)	violet	36.8	56
(E) Photochromatic Compound	2,455 (346 nm)	light blue	18.7	60

In Table II, the results obtained from the accelerated ageing tests in W-0-M are reported

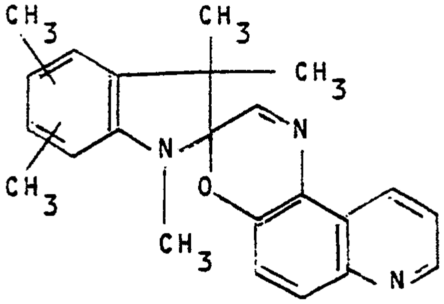
Table II

Photochromatic Compound/ Composition	Exposure in W-O-M (hours)					
	O.D.	(23°C)	O.D.	(23°C)	O.D.	(23°C)
(a) Composition	3.137	29.3	2.960	28.9	2.680	25.1
(b) Composition	3.097	32.2	2.845	32.2	2.530	26.9
(c) Composition	3.154	32.0	2.883	34.0	2.538	26.8
(A) Compound	1.610	33.0	0.800	21.8	0.380	9.0
(E) Compound	1.800	18.2	1.604	18.0	1.403	18.1

From an examination of these results, it is clear that the (a), (b) and (c) mixtures, with the photochromatic activity (Δ y), and the return times back to the deactivated status ($t_{1/2}$), being the same, show, as compared to the individual photochromatic (A) and (E) products, the advantages of a colour of the activated status which is more neutral, and can be modulated as a function of their ratio by weight; a considerably higher ageing strength and photochromatic activity then the pure (A) product, and the pure (E) product, respectively.

Example 2

The photochromatic response to sun light exposure is evaluated of a neutral lens of poly-diethylene-glycol-bis(allyl carbonate) impregnated with the (b) photochromatic mixture of Example 1, as compared to a similar lens impregnated with the spiro-oxazinic photochromatic compound known from the prior art, having the formula:



wherein the two methyl groups on the benzene-indolinic ring are in the 4,5- and 5,6-positions.

Both of them were activated by a 4-minute exposure to sun light, and were evaluated for the change in light transmittance (Δ y) shown by the two lenses following said exposure, and measured by means of the Gardner's Hazegard XL 211.

The results are reported in Table III.

Table III

Photochromatic Compound/ Composition	(b) Photochromatic Mixture	Spiro-Oxazine from the Prior Art
Optical density (λ_{max})	3.482 (350 nm)	1.792 (347 nm)
Activated status colour	gray-blue	blue
Deactivated status transmittance (%)	88	90
Activated status transmittance (%)	45	54
ΔY (%), at 23°C	43	54
$t_{1/2}$ (23°C, sec.)	50	110

As compared to the lens with the spiro-oxazine known from the prior art, the lens obtained with the (b) photochromatic mixture of the present invention shows a more neutral colour of the activated status, a higher photochromatic activity (Δ y), and a twice as high return rate to the deactivated status

Example 3

With the (b) photochromatic mixture of the previous example, a neutral photochromatic lens of poly-(methyl-methacrylate) is prepared, which has the following composition:

- (b) photochromatic mixture	10 mg	0.066 parts
- Methyl-methacrylate	15 g	100 parts
- Azo-bis(isobutyro-nitrile)	0.15 g	0.100 parts

The polymerization of the lens is carried out by casting, maintaining the mould in a temperature-controlled water bath at 55° C for 80 hours.

At the end of the polymerizazion, by opening the mould, a photochromatic lens of poly(methyl methacrylate) is obtained, which has the characteristics as reported in Tables IV and V.

In the same tables, also the characteristics are reported for comparison purposes, of lenses obtained, with the other conditions being the same, by separately using the individual (A) and (E) photochromatic compounds.

Table IV

Photochromatic Compound/ Composition	Optical Density (λ_{max})	Activated Status Colour	ΔY (23°C)	$t_{1/2}$ (23°C sec.)
(b) Composition	3.490 (349 nm)	gray-blue	26.0	28
(A) Compound	3.620 (363 nm)	violet	30.2	29
(E) Compound	3.020 (347 nm)	light blue	4.2	11

Table V

Photochromatic Compound/ Composition	Exposure in W-O-M (hours)					
	(O.D.)	ΔY ($23^{o}C$)	(O.D.)	ΔY ($23^{o}C$)	(O.D.)	ΔY ($23^{o}C$)
(b) Composition	3.312	20.9	3.306	19.5	3.268	17.6
(A) Compound	3.412	27.9	3.304	26.4	3.234	24.0
(E) Compound	2.402	3.8	1.620	3.0		

These results demonstrate that in poly-(methyl-methacrylate), the (b) composition according to the present invention unexpectedly shows photochromatic characteristics as well a stability, which are similar to those of the pure (A) photochromatic compound, even if it is constituted for its major portion by the (E) photochromatic compound, which, in the pure state, displays very bad photochromatic characteristics and ageing resistance.

Example 4

A mixture is prepared, which is constituted by a polypropylene powder of MOPLEN FLF 20 type, having a fluidity degree of 11, manufactured by HIMONT, and by the (b) photochromatic mixture of Example 1, in the mutual ratio by weight to each other of respectively 100:0.25.

For comparison purposes, mixtures of polypropylene with the individual (A) and (E) photochromatic compounds in the same weight ratios are prepared.

Said polymeric mixtures are transformed into films of 50 m of thickness by extrusion at the temperature of 215° C. The photochromatic characteristics of the so-obtained films, and the relevant resistances under such conditions as reported in the text, are reported in Table VI.

Table VI

Polypropylene film - Thickness 50 m - Photochromatic product concentration 0.1%

Photochromatic / Compound Composition	0 (O.D.)	ΔY 23°C	$t_{1/2}$ seconds	15 (O.D.)	ΔY 23°C	t1/2 seconds	30 (O.D.)	ΔY 23°C	$t_{1/2}$ seconds
(b) Composition	0.124	16.3	21	0.097	11.8	18	0.077	3.9	29
(A) Compound	0.169	18.4	22	0	0	/			
(E) Compound	0.100	4.2	10	0.08	0	/			

Example 5

A mixture of the (D) and (G) photochromatic compounds in the weight ratio of 60/40 is prepared.

Said mixture is applied by surface impregnation to neutral lenses of poly-diethylene-glycol-bis(allyl carbonate), and is evaluated as disclosed at Example 1.

The results are reported in Table VII.

Table VII

- Optical density (λ_{max})	2.944 (345 μm)
- Colour in the activated status	violet
- ΔY (23°C)	31.7
- $t_{1/2}$ (23°C, seconds)	55
- Ageing in W-O-M:	
- 52 hours, O.D.	1.728
ΔY (23°C)	24.8
- 85 hours, O.D.	1.450
ΔY (23°C)	19.2
- 158 hours, O.D.	1.077
ΔY (23°C)	18.1

Example 6

The following mixtures with a different weight ratio between the photochromatic compounds (A) and (F) are prepared:

Photochromatic Composition	1	2	3	4	5
(A) Compound	0	30	50	70	100
(F) Compound	100	70	50	30	0

The mixtures Nos. 1 and 5, are reported for comparative purposes.

Said mixtures were applied to the surface of neutral lenses of poly-diethylene-glycol-bis(allyl carbonate) according to the same technique as reported in Example 1.

The resulting properties are reported in Table VIII.

Table VIII

Composition No.	1	2	3	4	5
Optical density (λ_{max})	1.274	>4.500	2.600	1.378	2.006
Colour of the activated state	light blue	blue-violet	blue-violet	blue-violet	violet
ΔY 23°C	18.8	29.4	29.7	32.7	35.4
$t_{1/2}$, 23°C, seconds	20	32	34	40	42

The reported data shows the synergistic effect of the two (A) and (F) products, in that the photochromatic activity of their mixtures is very close to the photochromatic activity displayed by the more active (A) compound alone, and the times of return back to the deactivated form are considerably shorter.

The structures of a few photochromatic compositions of the invention are graphically illustrated in the accompagying drawings, wherein:

Figure 1 is an NMR¹H spectrogram of the photochromatic compound (A) at 10-5 δ;

Figure 2 is a spectrogram similar to that of Figure 1, but taken at 5-0 δ;

Figure 3 is an NMR'H spectrogram of the photochromatic composition (B);

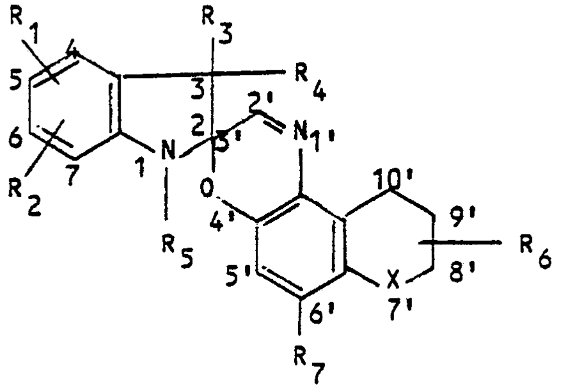
Figure 4 is an NMR¹H spectrogram of the photochromatic composition (C), and

Figure 5 is an NMR¹H spectrogram of the photochromatic composition (D).

For all the NMR¹H spectrograms shown in Figures 1-5, the substances to be tested were dissolved in deuterated chloroform.

Claims

1. Photochromatic composition of at least two photochromatic compounds, both of which can be represented by the following general formula (I):



(I)

wherein:

R_1 and R_2 independently represent a hydrogen atom or a halogen atom (chlorine, bromine or fluorine), or a group selected from: (C_1-C_5)-alkoxy; nitro; cyano; and a linear or branched (C_1-C_5)-alkyl either unsubstituted or substituted with one or more halogen (chlorine, bromine and fluorine) atoms, or (C_1-C_5)-alkoxy, (C_1-C_5)-alkyl-thio, (C_1-C_5)-carboxy-alkyl and cyano groups; or

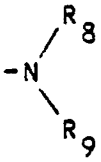
R_3 and R_4 independently represent linear or branched (C_1-C_5)-alkyl, phenyl or benzyl groups; or

R_3 and R_4, considered jointly, together with the carbon atom to which they are linked, form a (C_5-C_8)-cycloalkyl group;

R_5 is a phenyl; benzyl; allyl group; or a linear or branched (C_1-C_5)-alkyl group, either unsubstituted or substituted with one or more halogen (chlorine, bromine and fluorine) atoms, or (C_1-C_5)-alkoxy, (C_1-C_5)-alkyl-thio, (C_1-C_5)-carboxy-alkyl and cyano groups;

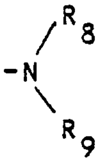
R_6 represents a hydrogen atom, a halogen (chlorine, bromine and fluorine) atom, or a group selected from (C_1-C_5)-alkoxy, (C_1-C_5)-alkyl-thio, (C_1-C_5)-carboxy-alkyl and cyano groups; and a linear or branched (C_1-C_5)-alkyl group, either unsubstituted or substituted with one or more halogen (chlorine, bromine and fluorine) atoms, or (C_1-C_5)-alkoxy, (C_1-C_5)-alkyl-thio, (C_1-C_5)-carboxy-alkyl and cyano groups; or represents a condensed aromatic or heterocyclic ring;

R_7 represents either a hydrogen atom, or an



; and

R_8 and R_9 represent, independently from each other, a hydrogen atom, or a linear or branched (C_1-C_5)-alkyl, phenyl or benzyl group; or
R_8 and R_9, when considered jointly with the nitrogen atom to which they are linked, form a mono-cyclic or poly-cyclic structure, of from 5 to 12 members, possibly containing a further heteroatom selected from between oxygen and nitrogen; and
X represents either a -CH- group or N;
in which composition at least one of the photochromatic compounds defined by the formula (I) is characterized in that it has the R_7 substituent constituted by hydrogen, and at least one of the photochromatic compounds defined by the formula (I) is characterized in that it has the R_7 substituent constituted by a group



wherein R8 and R9 have the above stated meanings.

2. Photochromatic composition according to claim 1, characterized in that in at least one of the compounds defined in formula (I), the substituents:
R_1 and R_2 independently represent the hydrogen atom, or the methyl, or methoxy groups;
R_3 and R_4 represent each the methyl or ethyl group, or, when considered jointly, represent the cyclohexyl group;
R_5 represents a (C_1-C_5)-alkyl group;
R_6 represents the hydrogen atom or the methoxy group;
R_7 represents an $-NR_8R_9$ group, wherein
R_8 and R_9 jointly represent, together with the nitrogen atom they are linked to, the piperidino, morpholino, pyrrolidinyl or hexamethylene-imino groups; and
X represents either -CH- or N.

3. Photochromatic composition according to claims 1 and 2, characterized in that the ratio by moles of the photochromatic compounds defined by formula (I) wherein R_7 is an $-NR_8R_9$ group to the compounds, also defined by formula (I), wherein R_7 is hydrogen, is a number comprised within the range of from 0.1 to 9.

4. Photochromatic composition according to claims 1 and 2, characterized in that the ratio by moles of the photochromatic compounds defined by formula (I) wherein R_7 is an $-NR_8R_9$ group to the compounds, also defined by formula (I), wherein R_7 is hydrogen, is a number comprised within the range of from 0.2 to 1.5.

5. Photochromatic composition according to the preceding claims, containing 1,3,3-trimethyl-6′-piperidino-spiro-[indolino-2,3′-(3H)-naphtho-(2,1 b)-(1,4)-oxazine].

6. Photochromatic composition according to claims from 1 to 4, containing 1,3,3-trimethyl-6′-morpholino-spiro-[indolino-2,3′-(3H)-naphtho-(2,1-b)-(1,4)-oxazine].

7. Photochromatic composition according to claims from 1 to 4, containing 1,3,3,4,5,- (or 1,3,3,5,6,-) pentamethyl-6′-piperidino-spiro-[indolino-2,3′-(3H)-naphtho-(2,1-b)-(1,4)-oxazine].

8. Photochromatic composition according to claims from 1 to 4, containing 1,3,3-trimethyl-6′-piperidino-9′-methoxy-spiro-[indolino-2,3′-(3H)-naphtho-(2,1-b)-(1,4)-oxazine].

9. Photochromatic composition according to claims from 1 to 4, containing 1,3,3,4,5- (or 1,3,3,5,6-) pentamethyl-spiro-[indolino-2,3′-(3H)-naphtho-(2,1-b)-(1,4)-oxazine].

10. Photochromatic composition according to claims from 1 to 4, containing 1,3,3-trimethyl-spiro-[indolino-2,3′-(3H)-naphtho-(2,1-b)-(1,4)-oxazine].

11. Photochromatic composition according to claims from 1 to 4, containing 1,3,3-trimethyl-9′-methoxy-spiro-[indolino-2,3′-(3H)-naphtho-(2,1-b)-(1,4)-oxazinie].

12. Photochromatic composition according to the preceding claims, characterized in that it contains an U.V.- stabilizer.

13. Photochromatic composition according to claim 9, characterized in that the U.V.-stabilizer is constituted by a sterically hindered amine (HALS).

14. Photochromatic article constituted by a transparent organic polymer, containing on its surface, or inside its mass, a photochromatic composition according to claims from 1 to 10.

15. Photochromatic article according to claim 14, characterized in that said transparent organic polymer is selected from poly-methyl-methacrylate, polyvinyl-alcohol, polyvinyl-pyrrolidone, cellulose acetate-butyrate, epoxy resins, polysiloxane resins, polyurethane resins, polycarbonate and poly-diethylene-glycol bis(allyl carbonate).

Fig.1

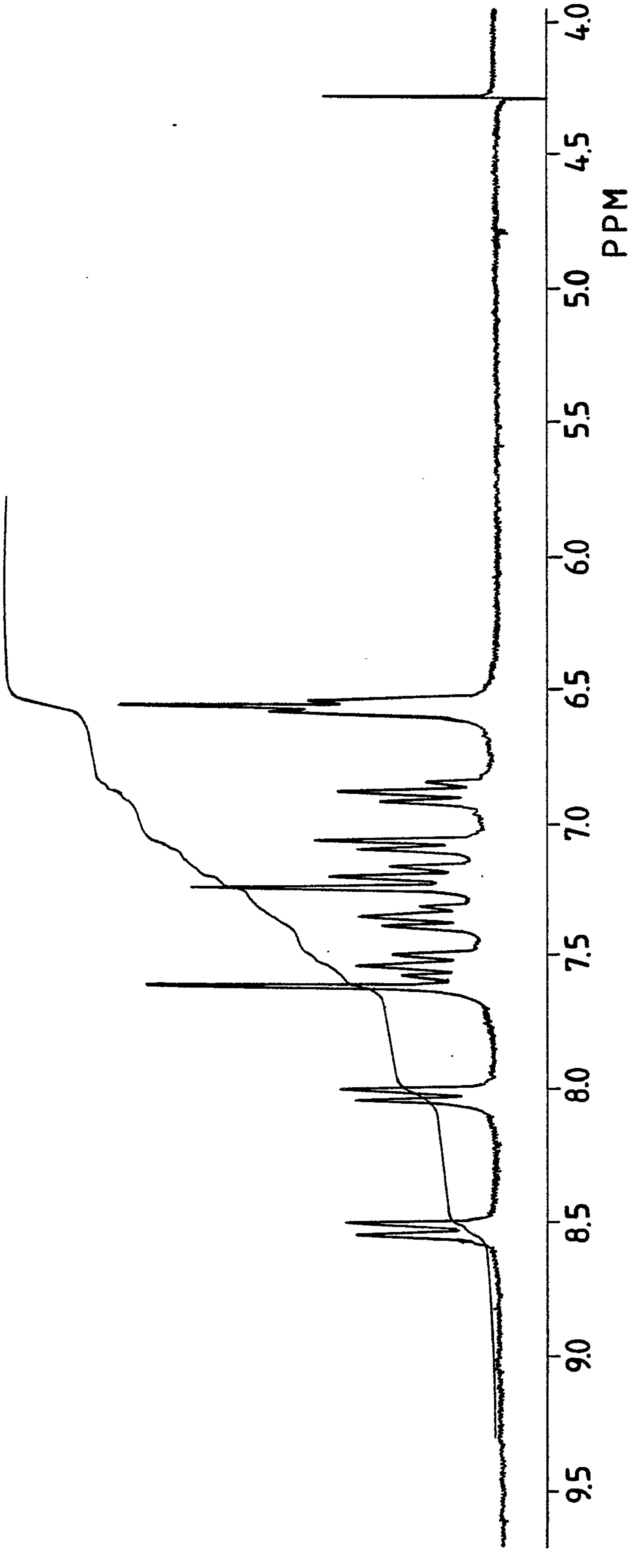
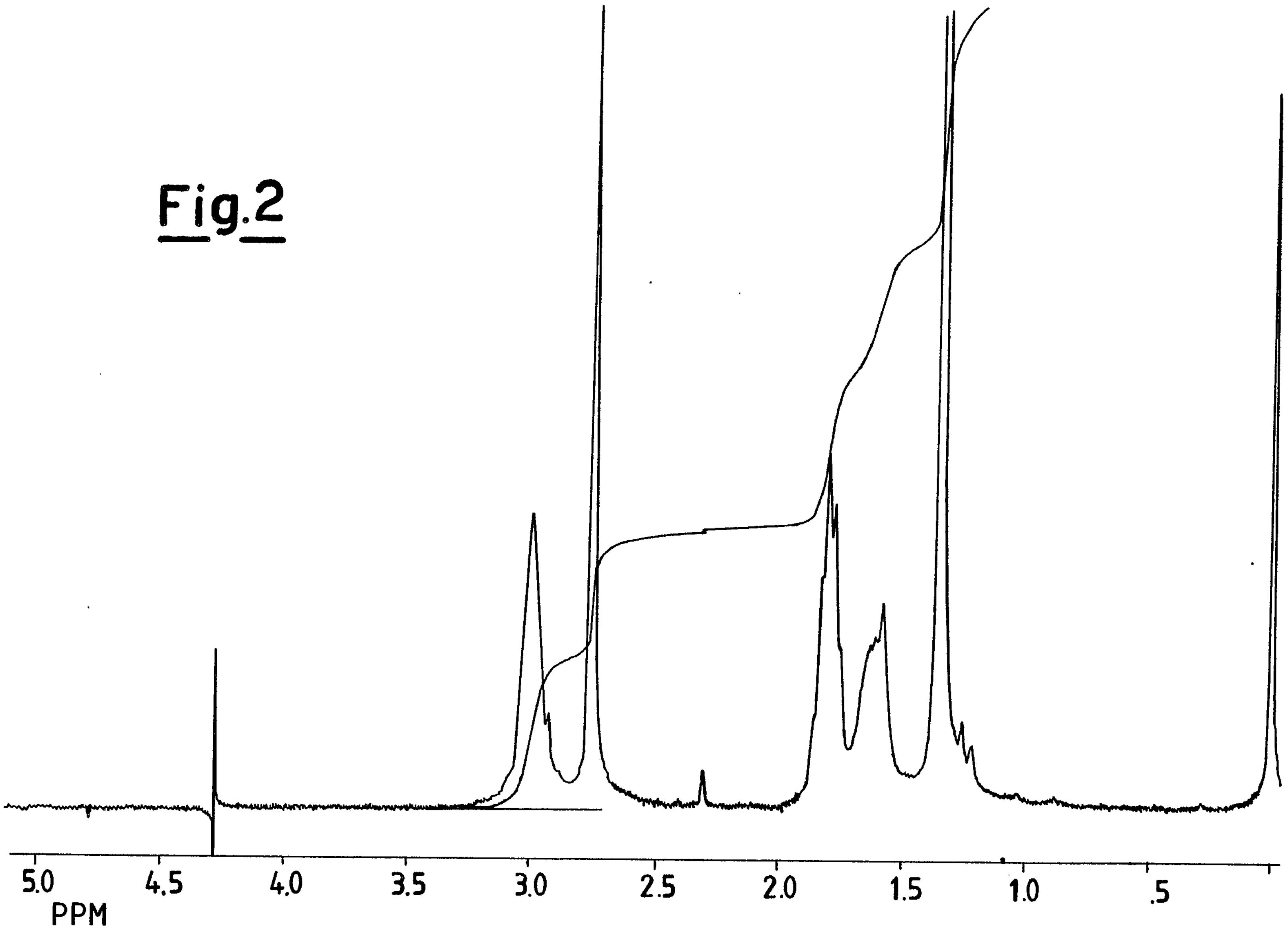


Fig.2



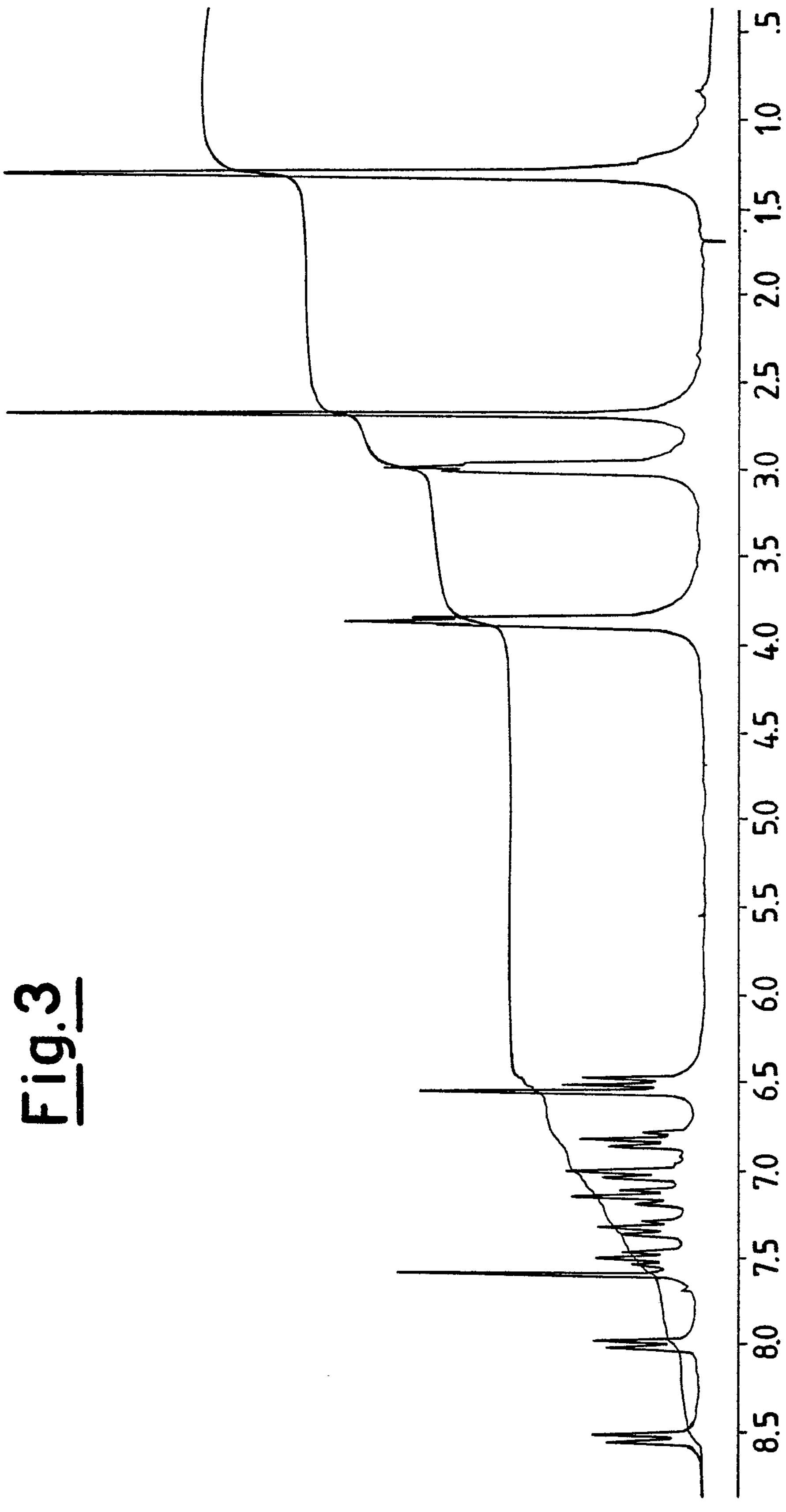


Fig.3

Fig.4

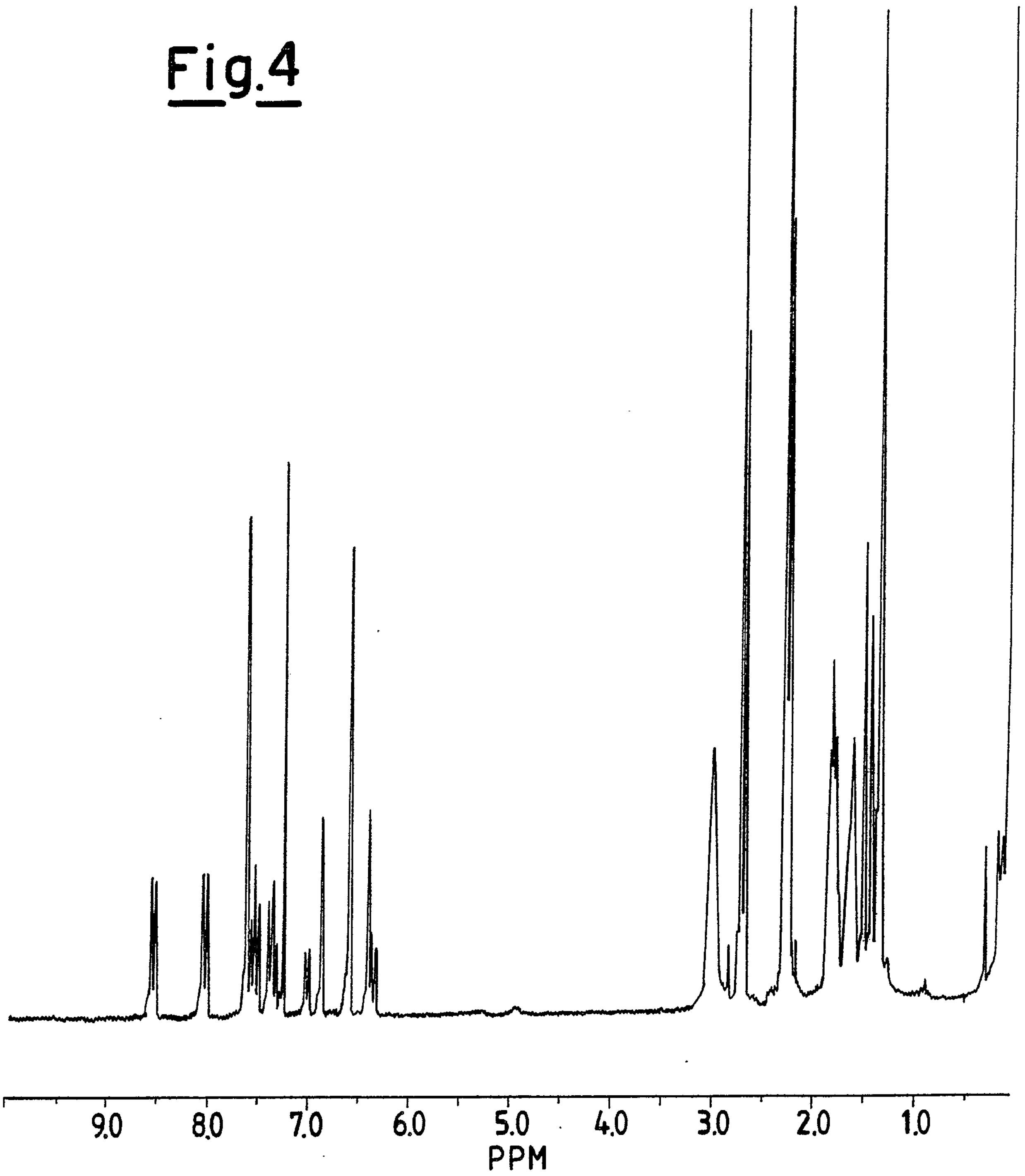
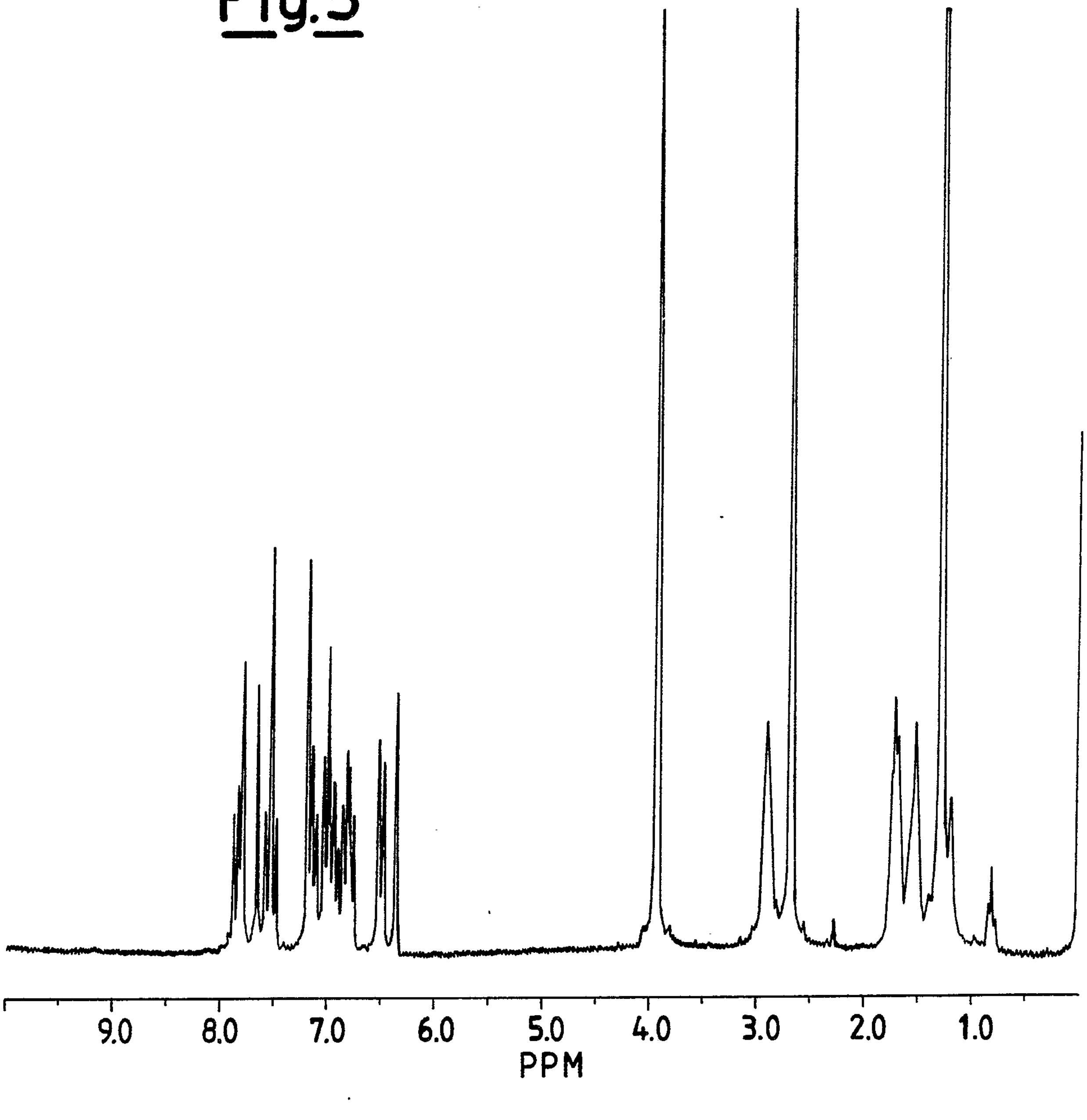


Fig.5



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EUROPEAN SEARCH REPORT

Application Number

EP 88 20 2408

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.4)
P,X D	EP-A-0 245 020 (PILKINGTON BROTHERS) * Claim 5 * ---	1-15	G 03 C 1/72
Y	EP-A-0 195 898 (AMERICAN OPTICAL CORP.) * Claim 1 * ---	1-15	
Y,D	US-A-4 342 668 (R.J. HOVEY et al.) * Claim 5 * -----	1-15	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

G 03 C 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	17-02-1989	DUPART J-M.B.

CATEGORY OF CITED DOCUMENTS

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