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(54) **Titre** : OBJET PHOTOCHROME EN PLASTIQUE A CONTRASTE INTENSIFIE DE MANIERE PERMANENTE
(54) **Title**: PHOTOCHROMIC PLASTIC OBJECT WITH PERMANENTLY INCREASED CONTRAST

(57) **Abrégé/Abstract**:

The invention relates to a photocromic plastic object, characterised by a permanently increased contrast relative to that of photocromic plastic objects available according to the state of the art. In other words, the photocromic plastic object according to the invention displays an improved contrast in the stationary state and in every phase, even during the darkening as well as during the lightening. Said plastic object can be used for as photocromic spectacle glass, in particular for sports glasses.

ABSTRACT

The invention relates to a photocromic plastic object, characterised by a permanently increased contrast relative to that of photocromic plastic objects available according to the state of the art. In other words, the photocromic plastic object according to the invention displays an improved contrast in the stationary state and in every phase, even during the darkening as well as during the lightening. Said plastic object can be used for as photocromic spectacle glass, in particular for sports glasses.

Photochromic Plastic Object with Permanently Increased Contrast

The present invention relates to a photochromic plastic object, characterized by a permanently increased contrast relative to that of photochromic plastic objects available according to the state of the art. That is, the photochromic plastic object according to the invention displays an improved contrast in the stationary state and in every phase, during darkening as well as during lightening. The inventive plastic object can be used as a photochromic lens for eyeglasses, particularly for sports glasses.

Photochromic plastic objects, in particular eyeglass lenses, have been commercially available since the 1980's. The first lens to find widespread distribution, for example Rodenstock Perfalit ColorMatic (since 1986) or the colored lens from Transitions Optical, Inc. (since 1990) marketed by several lens manufacturers as the Transitions lens, contained spirooxazines as photochromic dyes which darkened in a blue tint. Later products, such as the Transitions Plus gray lens (since 1992), the Transitions Eurobraun and Hoya Sunbrown brown lenses (since 1994), and the new Rodenstock Perfalit ColorMatic lens (since 1995) contained pyrans in addition to spirooxazines and/or fulgides. Products currently on the market, such as the Transitions III lens, preferentially use pyrans, specialized naphthopyrans, and larger ring systems derived therefrom. The Transitions III products having a refractive index of 1.56 are based on US Patent 5,753,146.

The lenses currently available according to the state of the art all have the common feature that said lenses do not exhibit satisfactory contrast on account of illumination-dependent darkening.

The object of the present invention, therefore, is to provide a photochromic plastic object characterized by a permanently increased contrast; that is, the photochromic plastic object displays an improved or increased contrast in the stationary state and in every phase, during darkening as well as during lightening. The inventive plastic object can be used in particular as a photochromic lens for eyeglasses such as sports glasses.

This object is achieved by the embodiments characterized in the claims.

In particular, a photochromic plastic object is provided that comprises a transparent plastic material and at least one photochromic dye incorporated therein, with the photochromic plastic object additionally having at least one agent that increases the contrast (contrast-increasing agent) and that absorbs in the visible light region of 380 nm to 500 nm in such a way that in the lightened state of at least one photochromic dye, the photochromic plastic object has an average transmission of at least 5%, up to a maximum of 30%, in the visible light region of 380 nm to 500 nm. In other words, in the lightened state of at least one photochromic dye, the photochromic plastic object according to the invention shows at least a 70% reduction in the average transmission in the visible light region of 380 nm to 500 nm.

In the lightened state of at least one photochromic dye, the photochromic plastic object preferably has an average transmission of 20% maximum, preferably 10% maximum, in the visible light region of 380 nm to 500 nm.

The photochromic plastic object according to the invention is characterized by a permanently improved or increased contrast, such that an improved contrast is created in the stationary state as well as during the darkening phase and during the lightening phase, which are brought about by the photochromic dye. This can be based in particular on the corresponding absorption of the contrast-increasing agent in the visible light region of 380 nm to 500 nm, whereby the shortwave blue portion of the incoming light is substantially filtered out. Due to the fact that the contrast between two objects is defined by the ratio of the difference between two luminances L_I and L_{II} to the sum thereof, and the luminance of blue scattered light is negligible, an increase in contrast cannot actually be objectively measured. However, a subjective impression is understood to be an increase in contrast within the scope of the present invention, as described in DOZ (Deutsche Optikerzeitung [German Opticians Journal]), 12/90, pp. 43 ff.

The shortwave blue portion of the incoming light is not entirely filtered out in the photochromic plastic object according to the invention, since otherwise an undesired color distortion, that is, a distortion of the color fidelity, would be created. Therefore, in the lightened state of at least one photochromic dye the photochromic plastic object has an average transmission of at least 5% in the visible light region of 380 nm to 500 nm. A low-level light in this spectral region is necessary to achieve high color fidelity.

Figure 1 shows the transmission curve for Celliton Orange R dye, marketed by BASF, in CR-39 plastic (commercial name: diethylene glycol bis(allyl carbonate), marketed by PPG Industries).

Figure 2 shows the transmission curve for a commercially available photochromic or phototropic plastic lens (Rodenstock ColorMatic Extra Grey) without the use of a contrast-increasing agent according to the invention. The transmission was recorded during illumination and lightening. The illumination time was 15 minutes, and irradiation was performed at 50 klux according to EN 1836, Section 6.1.3.1.1. Lightening took place in the dark.

Figure 3 shows the transmission curve for a photochromic plastic object according to the invention, in the form of a phototropic lens produced according to the example described hereinafter. The transmission was recorded during illumination and lightening. The illumination time was 15 minutes, and irradiation was performed at 50 klux according to EN 1836, Section 6.1.3.1.1. Lightening took place in the dark.

The photochromic plastic object according to the invention is especially suited as a photochromic lens for eyeglasses, for example sports glasses such as ski glasses. Of course, the photochromic plastic object according to the invention may also be used for all types of eyeglass lenses such as driving glasses and safety glasses, or for safety helmet visors, protective screens, windows, coverings, roofs, and the like.

The photochromic plastic object according to the invention contains one or more plastic materials as transparent plastic materials that act as a substrate or matrix for the photochromic dye(s) to be used. The plastic materials employed can be plastics commonly used in the state of the art, particularly for ophthalmological purposes. For example, the plastic material may be chosen from poly(C_1-C_{12} alkyl)methacrylates, polyoxyalkylene methacrylates, polyalkoxyphenolmethacrylates, cellulose acetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, polyvinyl acetate, polyvinyl alcohol, polyvinyl chloride, polyvinylidene chloride, polycarbonates, polyesters, polyurethanes, polyethylene terephthalate, polystyrene, poly-α-

methylstyrene, polyvinyl butyral, copoly(styrene-methylmethacrylate), copoly(styrene-acrylonitrile), and polymers composed of components of the group comprising polyol(allyl carbonate) monomers, polyfunctional acrylate, methacrylate, or diethylene glycol dimethacrylate monomers, ethoxylated bis-phenol-A-dimethacrylate monomers, diisopropenylbenzene monomers, ethylene glycol bis-methacrylate monomers, poly(ethylene glycol)bis-methacrylate monomers, ethoxylated phenolmethacrylate monomers, alkoxylated polyalcohol acrylate monomers, and diallylidene pentaerythritol monomers, or mixtures thereof.

In particular, the plastic material can be a solid, transparent homo- or copolymer chosen from the group comprising poly(methylmethacrylate), poly(ethylene glycol bis-methacrylate), poly(ethoxylated bis-phenol-A-dimethacrylate), thermoplastic polycarbonate, polyvinyl acetate, polyvinyl butyral, polyurethane, or a polymer chosen from components of the group comprising diethylene glycol bis(allyl carbonate) monomers, diethylene glycol dimethacrylate monomers, ethoxylated phenolmethacrylate monomers, ethoxylated diisopropenylbenzene monomers, and ethoxylated trimethylolpropanetriacrylate monomers.

The photochromic compounds used for the present invention are not subject to any specific restrictions. Said compounds are preferably chosen from the class of benzopyrans and higher annelated ring systems derived therefrom, especially naphthopyrans or fluorenopyrans. Thus, for example, [2H]-naphtho(1,2-b)pyrans aromatically or heteroaromatically substituted in the 2,2 position and also [3H]-naphtho(2,1-b)pyrans correspondingly substituted in the 3,3 position, such as naphthopyrans described in International Patent PCT-DE 98/02820 and indeno[2,1-f]naphtho[1,2-b]pyran derivatives and/or spiro-9-fluoreno[1,2-b]pyran derivatives described in International Patent PCT/EP 99/05258, may be used. Examples of such include the following:

3,13-diphenyl-3-(4-diphenylaminophenyl)-13-hydroxy-6-methoxyindeno[2,1-f]naphtho[1,2-b]pyran,
13-(2,5-dimethylphenyl)-3-(4-diphenylaminophenyl)-13-hydroxy-6-methoxy-3-phenylindeno[2,1-f]-naphtho[1,2-b]pyran,
13-(2,5-dimethylphenyl)-3-(4-diphenylaminophenyl)-13-hydroxy-3-

phenylindeno[2,1-f]naphtho[1,2-b]pyran,
Spiro-9-fluoreno-13'-{3-(4-dimethylaminophenyl)-6-methoxy-3-phenylindeno[2,1-f]naphtho[1,2-b]pyran},
Spiro-9-fluoreno-13'-{3-(4-dimethylaminophenyl)-3-phenylindeno[2,1-f] naphtho-[1,2-b]pyran},
Spiro-9-fluoreno-13'-{3-(4-diphenylaminophenyl)-6-methoxy-3-phenylindeno[2,1-f]naphtho[1,2-b]pyran},
Spiro-9-fluoreno-13'-{3-(4-diphenylaminophenyl)-3-phenylindeno[2,1-f] naphtho-[1,2-b]pyran},
Spiro-9-fluoreno-13'-{3-[4-(*N*-morpholinyl)phenyl]-6-methoxy-3-phenylindeno[2,1-f]naphtho[1,2-b]pyran},
Spiro-9-fluoreno-13'-{3-[4-(*N*-morpholinyl)phenyl]3-phenylindeno[2,1-f] naphtho[1,2-b]pyran},
Spiro-9-fluoreno-13'-{6-methoxy-3-phenyl-3-[4-(*N*-piperidinyl) phenyl]indeno[2,1-f]naphtho[1,2-b]pyran}, and
Spiro-9-fluoreno-13'-{3-phenyl-3-[4-(*N*-piperidinyl)phenyl]indeno [2,1-f]naphtho-[1,2-b]pyran}, and, for example,

3-(4-diphenylaminophenyl)-3-(2-fluorophenyl)-3H-naphtho[2,1-b]pyran,
3-(4-dimethylaminophenyl-3-(2-fluorophenyl)-3H-naphtho[2,1-b]pyran,
3-(2-fluorophenyl)-3-[4-(*N*-morpholinyl)phenyl]-3H-naphtho[2,1-b]pyran,
3-(2-fluorophenyl)-3-[4-(*N*-piperidinyl)phenyl]-3H-naphtho[2,1-b]pyran,
3-(4-dimethylaminophenyl)-6-(*N*-morpholinyl)-3-phenyl-3H-naphtho [2,1-b]pyran,
6-(*N*-morpholinyl)-3-[4-(*N*-morpholinyl)phenyl]-3-phenyl-3H-naphtho [2,1-b]pyran,,
6-(*N*-morpholinyl)-3-phenyl-3-[4-(*N*-piperidinyl)phenyl]-3H-naphtho [2,1-b]pyran,
6-(*N*-morpholinyl)-3-phenyl-3-[4-(*N*-pyrrolidinyl)phenyl]-3H-naphtho [2,1-b]pyran,
3-phenyl-3-(2-fluorophenyl)-3H-naphtho[2,1-b]pyran,
6-(*N*-morpholinyl)-3,3-diphenyl-3H-naphtho[2,1-b]pyran, and
6-(*N*-morpholinyl)-3-(4-methoxyphenyl)-3-phenyl-3H-naphtho[2,1-b]pyran. However, the pyrans described in US Patent 5,753,146 and European Patent Application A-0 562 915, in addition to photochromic

dyes of other classes such as oxazines, as described for example in US Patent 5,753,146, or fulgides may also be used.

In a preferred embodiment of the present invention, the contrast-increasing agent may be a dye chosen from the group comprising organic dyes and pigments, or may be designed as a reflective coating or an absorbent coating, or may be a combination of two or more thereof.

When an organic dye is provided as a contrast-increasing agent in one embodiment, said dye may be chosen from the group of azo dyes, polymethyne dyes, arylmethyne dyes, polyene dyes, and carbonyl dyes. Examples of organic dyes that may be used within the scope of the present invention as contrast-increasing agents, and which correspondingly absorb in the visible light region of 380 nm to 500 nm, include Celliton Orange R and Celliton Yellow 7GFL marketed by BASF, Resolin Brilliant Yellow PGG marketed by Bayer, Samaron Brilliant Orange GSL marketed by Dystar (formerly Hoechst), Terasil Orange R marketed by Ciba-Geigy, and Dorospers Orange R marketed by Dohmen. Figure 1 shows an example of the transmission curve for Celliton Orange R dye in CR-39 plastic (commercial name: diethylene glycol bis(allyl carbonate), marketed by PPG Industries).

When in another embodiment a pigment is provided as a contrast-increasing agent, the pigment may be an inorganic or organic pigment.

In a further embodiment, the contrast-increasing agent may be provided as a reflective coating on the transparent plastic material, which incorporates at least one photochromic dye. According to the present invention, this reflective coating is subject to no restrictions regarding the material used, as long as said reflective coating is designed such that the photochromic plastic object in the lightened state of at least one photochromic dye has an average transmission of 30% maximum in the visible light region of 380 nm to 500 nm. Such a reflective coating is preferably designed as a multilayer structure in which metal oxides such as SiO_2, ZrO_2, TiO_2, Al_2O_3, HfO_2, and Ta_2O_5, or metal fluorides such as MgF_2, may be used as materials. For example, such a reflective coating may be formed from seven alternating, high- or low-refractive layers (7 $\lambda/4$ layers) of TiO_2 or SiO_2 and a $\lambda/2$ protective layer of SiO_2, where for example the thickness of the $\lambda/4$ TiO_2 layer is 48 nm, the thickness of the λ/4 SiO_2 protective layer is 74 nm, and the thickness of the λ/2 SiO_2 protective layer is 148 nm, where λ stands for light having a wavelength of 440 nm. Such a reflective coating with a multilayer design may be created by known physical vapor deposition (PVD) methods, for example.

In a further embodiment, the contrast-increasing agent may be provided as an absorbent coating on the transparent plastic material, which incorporates at least one photochromic dye. According to the present invention, this absorbent coating is subject to no restrictions regarding the material used, as long as said absorbent coating absorbs in the visible light region of 380 nm to 500 nm such that the photochromic plastic object in the lightened state of at least one photochromic dye has an average transmission of 30% maximum in the visible light region of 380 nm to 500 nm. Such an absorbent coating may have a multilayer design in the sequence $TiO_2/SiO_2/TiO_2/SiO_2/...$, having one or more metal layers such as Cr, Ag, or Cu layers instead of a corresponding TiO_2 or SiO_2 layer, or said absorbent coating may be formed as a single layer from a dielectric matrix, such as SiO_2, having one or more colorants such as Mo, WO_x, or FeO_x, for example, or one or more organic dyes incorporated therein.

The photochromic plastic object according to the invention may also have one or more hardcoat layers for improved scratch resistance. Furthermore, one or more conventional anti-reflective coatings may be provided on the side of the plastic object facing toward the light.

The photochromic plastic object according to the invention may be produced by various methods. In principle, photochromic plastic lenses may be produced in three different ways. For one, the photochromic dyes may be homogeneously distributed in the body of the plastic lens. Alternatively, the photochromic dyes may be incorporated in the surface (generally only on the convex side) of the plastic lens by diffusion, using heat. The photochromic dyes may also be applied in a layer on the plastic lens.

When the contrast-increasing agent is provided in the form of an organic dye, one or more organic dyes that are suitable for filtering out the shortwave blue portion of the incoming light to increase the contrast may be added to the plastic materials—for one, during production of the plastic object—in addition to at least one photochromic dye. Such mass coloration encompasses, for example, the dissolution or dispersion of at least one appropriate photochromic compound and at least one organic dye in a plastic material, such as by addition of the compounds to a monomeric material before the polymerization is carried out. In the case of mass coloration, that is, addition of the photochromic dyes and the organic dye as a contrast-increasing agent before the polymerization, said photochromic and organic dyes may be added to the finished casting resin (monomers, initiator, any additives such as antioxidants, and UV absorber), preferably in a concentration of 0.01 to 0.1 wt%, preferably 0.03 to 0.06 wt%, for example, and preferably in proportions of photochromic dye(s)/organic dyes(s) equal to 1 to 10 wt%, relative to the weight of the photochromic dye.

On the other hand, at least one organic dye together with at least one photochromic dye may be incorporated into the plastic material by diffusion in a dye bath. However, a decrease in photochromism sometimes occurs with this method. This can be avoided by diffusing the appropriate photochromic compound after the contrast-increasing agent, which is in the form of the organic dye. In addition to the dye concentration, the key factors in the production of diffusion-dyed lenses are the specialized plastic matrix used, the diffusion rate, and the depth of penetration of the dyes. The dyeing time, dyeing temperature, and polymerization conditions of the plastic lens are important as well. When the permeation of plastic material(s) along with the photochromic compound(s) and the contrast-increasing agent in the form of an organic dye is carried out by immersing the plastic material in a hot solution of the photochromic dye(s) and the contrast-increasing agent, or by a thermal transfer method, for example, the corresponding organic dye used must have an "absorption hole," that is, the site where absorption is lowest, in the region where the photochromic dye simultaneously used has an absorption maximum. The term "permeation" refers to the migration of the photochromic compound(s) and at least one organic dye used as the contrast-increasing agent into the plastic material, for example by the solvent-mediated transfer of the photochromic compound(s) into a polymer matrix, by vapor phase transfer, or other such surface diffusion methods.

When a pigment is provided as the contrast-increasing agent, and said pigment filters out the shortwave blue portion of the incoming light to increase the contrast, the pigment may be applied as a separate lacquer layer on the plastic object according to the invention, specifically, on the side of the plastic object facing away from the light so as not to impair darkening and lightening of the photochromic object.

Alternatively, application of the photochromic compound(s), and thus the photochromic effect, may also be achieved in the form of a separate lacquer layer on the plastic material already provided with an organic dye as the contrast-increasing agent. Of course, the contrast-increasing agent in the form of an organic dye or pigment may also be applied in an additional lacquer layer on the side of the plastic object facing away from the photochromic lacquer layer. This also applies to the contrast-increasing agent in the form of an absorbent coating. When the photochromic compound(s) is/are applied as part of a coating on the surface of the plastic material, the concentration depends on the thickness of the coating. For example, for a coating thickness of 20 μm, 2 wt% has been found to be suitable, and for a coating thickness of 40 μm, 1 wt% is suitable.

When the contrast-increasing agent is provided in the form of a reflective coating or an absorbent coating, this coating is usually subsequently applied to the plastic material having at least one photochromic dye, whereby a bonding layer such as an SiO or Cr layer may optionally be provided in a thickness that does not impair the optical properties of the plastic object according to the invention.

The present invention is explained in more detail in the following example.

Example

A Perfalit ColorMatic Extra Grey plastic lens from Rodenstock was used as the transparent photochromic plastic material. A permanent dye, namely Dorospers Orange R dye from Dohmen, was used as the contrast-increasing agent according to the invention. The lens was covered on the convex side so that no diffusion could occur from that side. The lens was then placed in a dye bath containing the aforementioned dye in deionized water, using BS dispersant from Dohmen (concentration: 10 g Dorospers Orange R dye and 40 mL BS dispersant in 5 liters deionized water; temperature approximately 90□C; dyeing time approximately 5 minutes). The covering was subsequently removed and the lens was cleaned by customary means.

Figure 3 shows the transmission curve of the phototropic lens thus obtained, with the transmission recorded during illumination and lightening. The illumination time was 15 minutes, and irradiation was performed at 50 klux according to EN 1836, Section 6.1.3.1.1. Lightening took place in the dark. Compared to the transmission spectrum shown in Figure 2 for a commercially available photochromic or phototropic plastic lens (Rodenstock ColorMatic Extra Grey) without using a contrast-increasing agent according to the invention, the transmission spectrum represented in Figure 3 shows a drastic reduction in the average transmission in the visible light region of 380 nm to 500 nm, which is caused by a corresponding absorption of the contrast-increasing agent in the form of Dorospers Orange R permanent dye in the visible light region of 380 nm to 500 nm. Consequently, the shortwave blue portion of the incoming light is substantially filtered out, resulting in a permanently increased contrast.

Claims

1. Photochromic plastic object comprising a transparent plastic material and at least one photochromic dye incorporated therein, with the photochromic plastic object additionally having at least one agent that increases the contrast and that absorbs in the visible light region of 380 nm to 500 nm in such a way that in the lightened state of at least one photochromic dye, the photochromic plastic object has an average transmission of at least 5%, up to a maximum of 30%, in the visible light region of 380 nm to 500 nm.

2. Photochromic plastic object according to Claim 1, characterized in that in the lightened state of at least one photochromic dye, the photochromic plastic object has an average transmission of 20% maximum, preferably 10% maximum, in the visible light region of 380 nm to 500 nm.

3. Photochromic plastic object according to Claim 1 or 2, characterized in that the contrast-increasing agent is a dye chosen from the group comprising organic dyes and pigments, or is designed as a reflective coating or an absorbent coating, or is a combination of two or more thereof.

Fig. 1

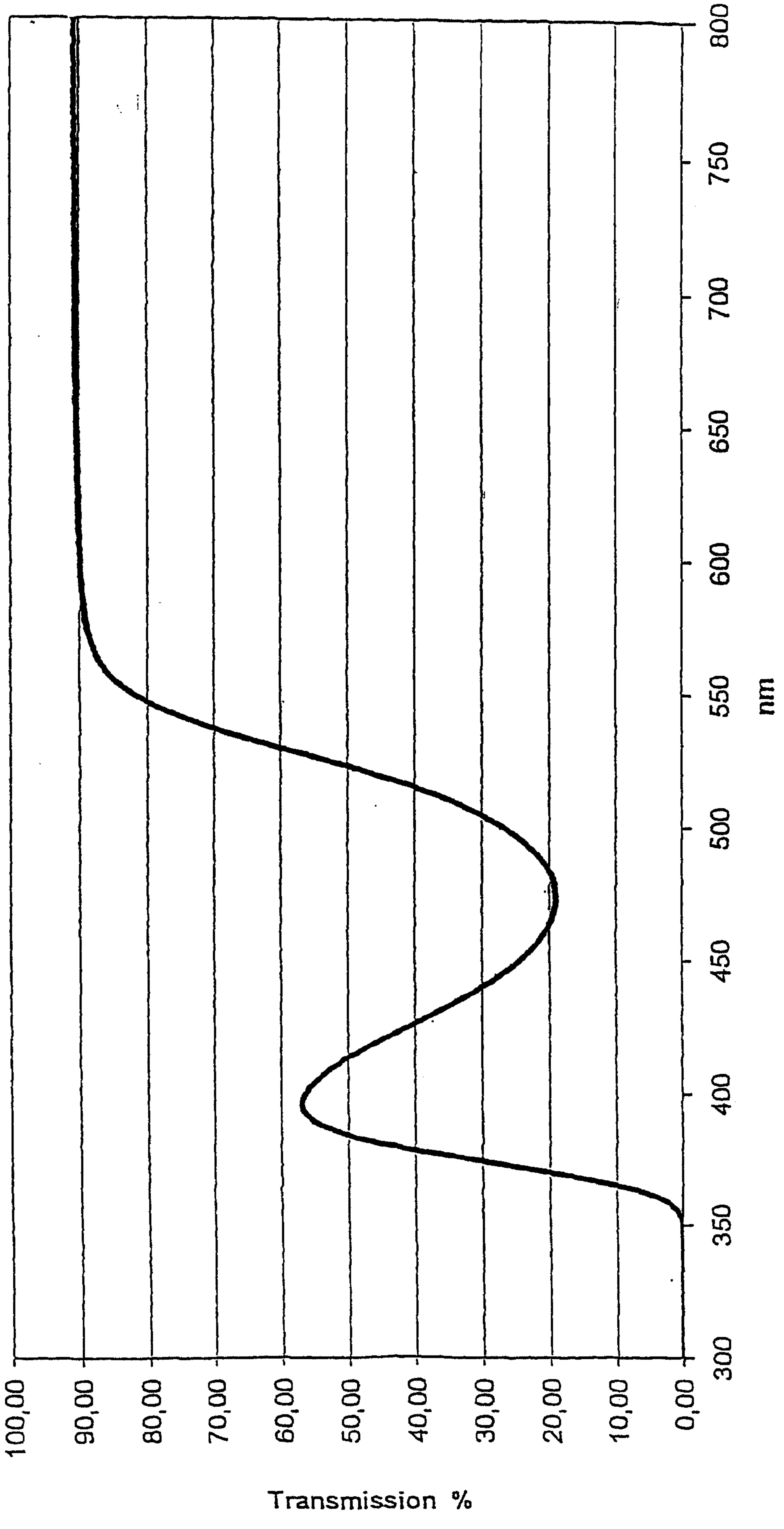

800
750
700
650
600
550
500
450
400
350
300
nm
100,00
90,00
80,00
70,00
60,00
50,00
40,00
30,00
20,00
10,00
0,00
Transmission %

Fig. 2

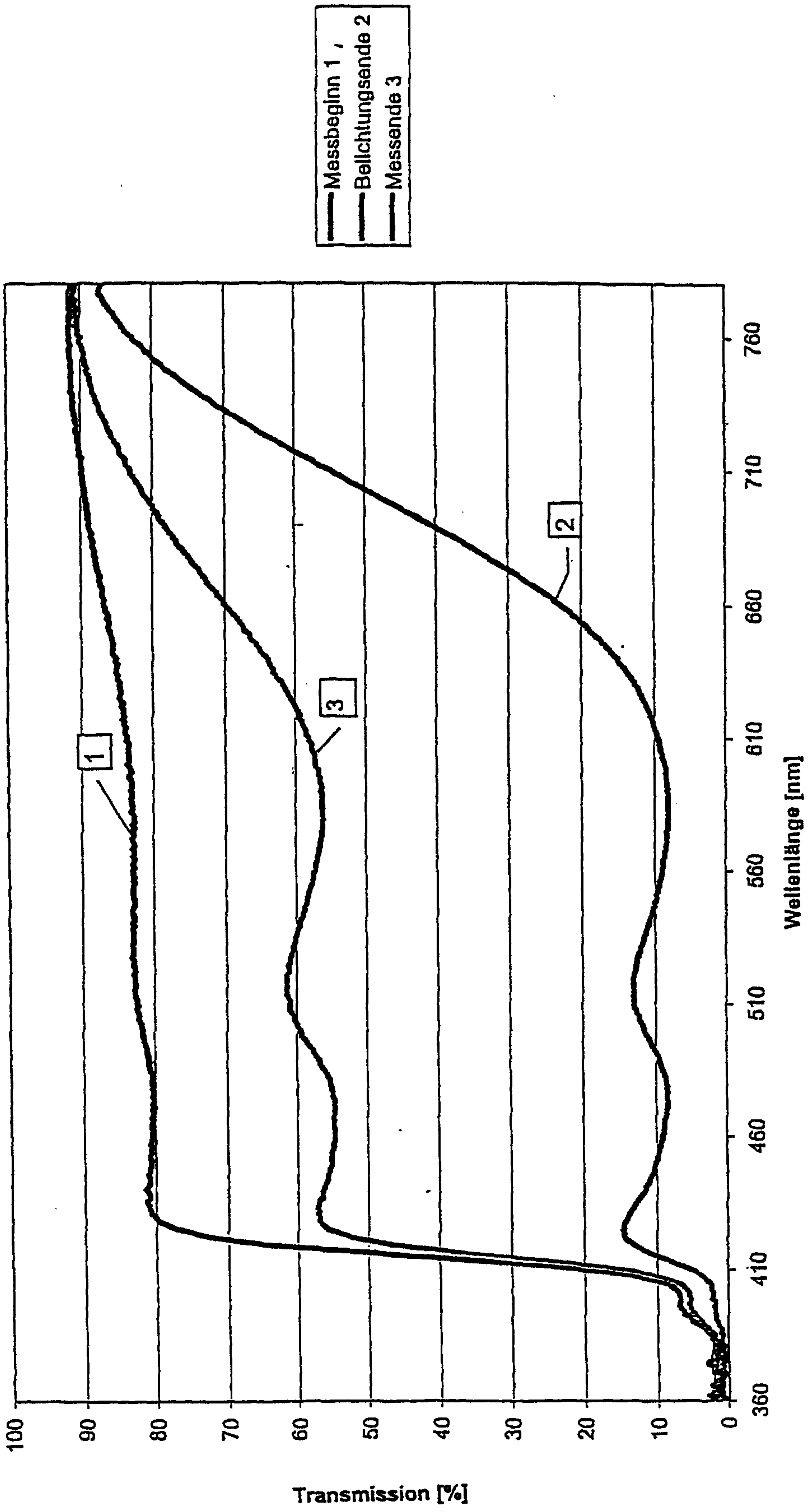
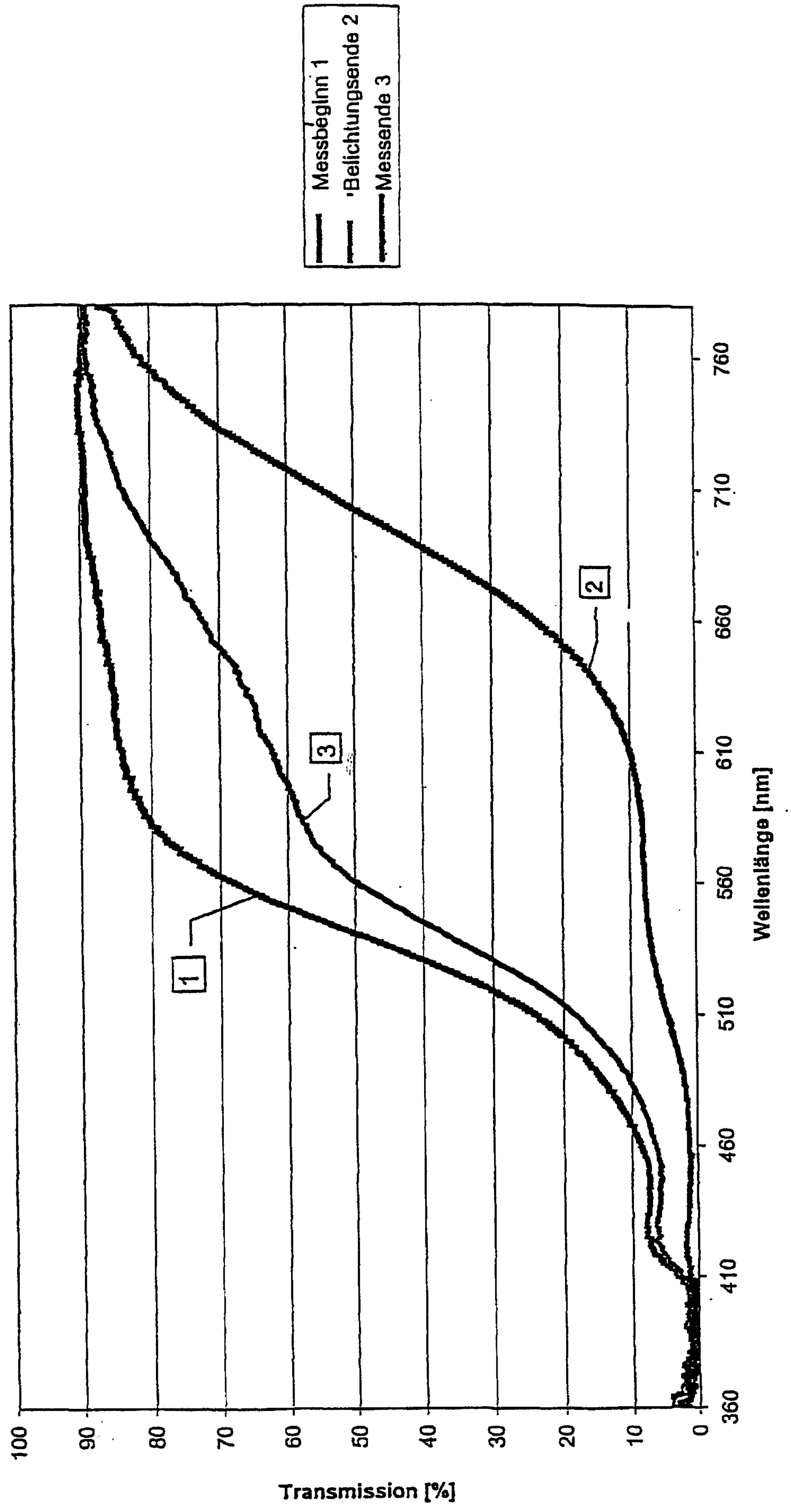

Messbeginn 1
Belichtungsende 2
Messende 3
1
2
3
Transmission [%]
100
90
80
70
60
50
40
30
20
10
0
Wellenlänge [nm]
360
410
460
510
560
610
660
710
760

Fig. 3


Messbeginn 1
Belichtungsende 2
Messende 3
Transmission [%]
0
10
20
30
40
50
60
70
80
90
100
Wellenlänge [nm]
360
410
460
510
560
610
660
710
760
1
2
3

Figures 2, 3

Wellenlänge = wavelength
Messbeginn = beginning of measurement
Belichtungsende = end of illumination
Messende = end of measurement