COMMONWEALTH of AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

~~I~~
We FLACHGLAS AKTIENGESELLSCHAFT, of

Otto-Seeling-Promenade 10-14,
D-8510 Furth/Bayern,
Federal Republic of Germany.

hereby apply for the grant of a Standard Patent for an invention entitled:

"PROCESS FOR THE MANUFACTURE OF A TOUGHENED AND/OR BENT SHEET OF GLASS, IN PARTICULAR SOLAR CONTROL GLASS SHEET"

which is described in the accompanying ~~provisional~~ complete specification.

Details of basic application(s):—

Number	Convention Country	Date
P 36 28 051.8-45	Federal Republic of Germany	19th August 1986

APPLICATION ACCEPTED AND AMENDMENTS
ALLOWED 21-11-89

LODGED AT SUB-OFFICE
19 AUG 1987
Melbourne

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

Dated this 18th day of August 1987

H. W. Rimington

To: THE COMMISSIONER OF PATENTS

....
(a member of the firm of DAVIES & COLLISON for and on behalf of the Applicant).

Davies & Collison, Melbourne and Canberra.

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

DECLARATION IN SUPPORT OF CONVENTION OR NON-CONVENTION APPLICATION FOR A PATENT

Insert title of invention.

In support of the Application made for a patent for an invention entitled: "PROCESS FOR THE MANUFACTURE OF A TOUGHENED AND/OR BENT SHEET OF GLASS, IN PARTICULAR SOLAR CONTROL GLASS SHEET"

Insert full name(s) and address(es) of declarant(s) being the applicant(s) or person(s) authorized to sign on behalf of an applicant company.

WE ~~I~~X ~~We~~ Werner Geiser and Helmut Böttge

of FLACHGLAS AKTIENGESELLSCHAFT,
of Otto-Seeling-Promenade 10-14,
D-8510 Furth/Bayern,
Federal Republic of Germany

Cross out whichever of paragraphs 1(a) or 1(b) does not apply

1(a) relates to application made by individual(s)

1(b) relates to application made by company; insert name of applicant company.

do solemnly and sincerely declare as follows :-

~~1. (a) I am / We are the applicant.......... for the patent~~

or (b) I am authorized by

FLACHGLAS AKTIENGESELLSCHAFT

the applicant............. for the patent to make this declaration on its ~~their~~ behalf.

Cross out whichever of paragraphs 2(a) or 2(b) does not apply

2(a) relates to application made by inventor(s)

2(b) relates to application made by company(s) or person(s) who are not inventor(s); insert full name(s) and address(es) of inventors.

~~2. (a) I am / We are the actual inventor.......... of the invention~~

or (b) Dr. Franz-Josef Schmitte, of Rudolfstr. 1
4650 Gelsenkirchen, Germany

is ~~are~~ the actual inventor........... of the invention and the facts upon which the applicant........... is ~~are~~ entitled to make the application are as follows :-

State manner in which applicant(s) derive title from inventor(s)

Unlimited claiming in accordance with the provisions of the German Law concerning inventions made by employees, whereby the applicant would, if a patent were granted upon an application made by the said actual inventor, be entitled to have the patent assigned to it.

Cross out paragraphs 3 and 4 for non-convention applications. For convention applications, insert basic country(s) followed by date(s) and basic applicant(s).

3. The basic application........... as defined by Section 141 of the Act was ~~were~~ made

in Federal Republic of Germany on the 19th August, 1986

by Flachglas Aktiengesellschaft

in .... on the ....

by ....

in .... on the ....

by ....

4. The basic application......... referred to in paragraph 3 of this Declaration was ~~were~~ the first application.......... made in a Convention country in respect of the invention the subject of the application.

Insert place and date of signature.

Declared at Fürth this 21st day of October 1987

Signature of declarant(s) (no attestation required)

Note: Initial all alterations.

FLACHGLAS AKTIENGESELLSCHAFT

ppa. [signature] ppa. [signature]

DAVIES & COLLISON, MELBOURNE and CANBERRA.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-77221/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 593385

(54) Title
LIGHT ABSORBING COATING ON THERMALLY TOUGHENED GLASS

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(56) Prior Art Documents
US 4715879

(57) Claim

1. Process for the manufacture of a toughened and/or bent sheet of soda-lime silica glass with reduced transmission, in particular solar control glass sheet, in which at least on one side of a transparent glass base at least one transmission-reducing coating with a considerable content of a metal or a metal alloy made of the elements with atomic numbers 22 to 28 in the periodic system is applied in such a thickness that the light transmission of the glass base provided with the transmission-reducing coating is between 10 and 90% of that of the glass base alone, and a thermal toughening and/or bending process is carried out in air at a temperature of 580°C to 680°C, preferably 600°C to 650°C, characterised by the fact that the transmission-reducing coating is produced by means of magnetron cathodic sputtering before the thermal toughening and/or bending process by the joint application of the metal or the metal alloy from the elements with atomic numbers 22 to 28 and silicon as a metal silicide coating with a silicon content of at least 45 atom %.

COMMONWEALTH OF AUSTRALIA

PATENT ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE

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Application Number:
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Complete Specification Lodged:
Accepted:
Published:

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Related Art:

This document contains the amendments made under Section 49 and is correct for printing.

NAME OF APPLICANT: FLACHGLAS AKTIENGESELLSCHAFT

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NAME(S) OF INVENTOR(S) Franz-Josef SCHMITTE

ADDRESS FOR SERVICE: DAVIES & COLLISON, Patent Attorneys
1 Little Collins Street, Melbourne, 3000.

COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

"PROCESS FOR THE MANUFACTURE OF A TOUGHENED AND/OR BENT SHEET OF GLASS, IN PARTICULAR SOLAR CONTROL GLASS SHEET"

The following statement is a full description of this invention, including the best method of performing it known to us :-

GERMAN PATENT

FLACHGLAS AKTIENGESELLSCHAFT, Otto Seeling Promenade

Process for the manufacture of a toughened and/or bent sheet of glass, in particular solar control glass sheet

The invention relates to a process for the manufacture of a toughened and/or bent sheet of soda-lime silica glass with reduced transmission, in particular solar control glass sheet, in which on at least one side of a transparent glass base at least one transmission-reducing coating with a considerable content of a metal or a metal alloy made of elements with the atomic numbers 22 to 28 in the periodic system is applied in such a thickness that the light transmission of the glass base provided with the transmission-reducing coating is between 10 and 90% of that of the glass base alone, and a thermal toughening and/or bending process is carried out in air at a temperature of 580 °C to 680°C, preferably 600°C to 650°C.

Sheets of glass which have a coating made of a metal or a metal alloy on their surface are used in the building sector and in automotive glazing in order to reduce the transmission of the uncoated glass base in certain spectral ranges. This takes places for example in order to achieve a light subduing effect and/or a solar control effect. In connection with this, preferably metals or metal alloys are used for the metal coating with atomic numbers 22 to 28 in the periodic system, if sheets of glass are required in which the coating does not affect the colour considerably in transmission and reflection. Thus generally the conventional soda-lime silica glass is used as a glass base. This can, in addition, be mass-tinted, as is the case with bronze, grey and green glass. As the result of this mass-tinting, there is already a basic solar control effect, which is intensified in addition by the coating. In particular in the case of glazing of motor vehicles, mass-tinted green glasses are frequently used, which distinguish themselves by a good solar control effect in conjunction with high light transmission. With such applications, mixed glazings are particularly interesting, whereby part of the sheet of glass is additionally coated. Thus for example the front light and the front side lights, upon which extensive legal provisions with regard to the minimum light transmission are placed, are fitted with mass-tinted green glass. For the rear area of the vehicle, for which lower light transmission values are permissible, the same mass-tinted lights are used, which however are additionally coated in order to further increase the solar control effect. In many applications including the type described above it is necessary to thermally toughen the glass base. The temperature necessary for this is in the region of 580°C to 680°C, preferably in the region of 600 to 650°C. The same temperature range is also required when the sheets of glass, coming flat from glass production are subjected to a bending process, whereby until now the application of the above-named neutral coloured coatings has taken place after the toughening or bending process and cooling of the glass lights has been concluded..

This procedure, namely carrying out the coating process after the toughening or bending process, has various disadvantages compared with a working method in which initially the coating is applied and then the toughening or bending process is carried out. Thus in the first case only cut sizes can be coated, as it is known that toughened glass lights cannot be cut to size. A further disadvantage with the procedure used until now lies in the fact that as a result of the high temperatures of the toughening or bending process impurities on the surface of the glass are frequently bonded so firmly to the latter that in the subsequent surface cleaning before carrying out the coating process they can no longer be removed to the degree which would be desirable for the subsequent coating process. A process in which flat glass, in particular in the form of unit dimensions, could be initially coated and then toughened or bent would on the other hand have considerable advantages. This procedure has, however, not been possible until now for coatings made of metals or metal alloys of elements with atomic numbers 22 to 28 preferably used on account of colour neutrality, because disturbing changes in the coating - in particular as a result of oxidation of the coatings - are caused by the temperatures required above 580°C. This is, for example, described in DE-OS 17 71 223, from which it is apparent that metal coatings of the type described above are oxidised as a result of a heat treating stage at temperatures of between 350°C and 677.55°C, as a result of which the transmission of the coatings is increased in particular in the near infra red and thus the solar control effect deteriorates in an undesirable way compared with those of non-oxidised metal coatings. Also in the case of a combination of metal coatings of the type described above with transparent oxide coatings, as for example described in US-PS 38 46 152, adequate stability to temperature stressing as occurs during the toughening or bending process cannot be achieved.

In order to overcome the difficulties referred to above and to protect the named metals or metal alloys from oxidation during the toughening or bending process, it has already been suggested (German Patent Application P 35 44 840.7-45) that a metal oxide coating with a defined oxygen deficit is applied on to the metal or metal alloy coating in a thickness of 10 nm to 100 nm, whereby during the toughening or bending process no notable oxygen diffusion to the metal or metal alloy coating can take place. This solution has admittedly proven itself in principle, does however require that in addition to the metal or metal alloy coating in a way which is difficult to control from the point of view of the process a sub-stochiometric oxide coating must be applied, which increases in an undesirable manner the reflection capacity of the coated sheet seen from the glass side or at least destroys again the anti-reflection effect of the one contact surface which arises as a result of the application of the metal or metal alloy coating.

It is already known (DE-PS 25 26 209) how to produce coatings made of silicon for solar controlled purposes on glass, whereby these coatings have a dark brown tinted view in transmission and a high reflection capacity of more than 50%, which is also not changed by a toughening process. For applications in the automotive sector, such coating systems are therefore not suitable on account of the existing legal provisions on the reflection of the glass lights towards the outside.

From DE-OS 21 38 034 it is in addition also known how to produce solar control coatings by using nitrides, carbides and silicides of elements of the groups IV, V and VI and thus also elements with atomic numbers 22 to 28 in the periodic system, which are relatively resistant to corrosion and in the case of chromium silicide are also highly resistant to scratching (see US-PS 40 51 297). The above silicide coatings which were produced by DC or HF cathodic sputtering, had, however, a strong colour shift in transmission, as is apparent in the examples described in DE-OS 21 38 034, so that for applications in which neutral-coloured, transmission-reducing coatings are required they are unsuitable. From the current stand point, it can be assumed that the coatings described here have a relatively high oxide content caused by the process, which had probably caused the colour shift. Any reference to the behaviour of these coatings during bending and/or toughening of sheets of glass coated in this way is not apparent from the above patent application.

The invention therefore aims to develop the process of the type described at the beginning in such a way that the above disadvantages are all avoided and in a simple, reproducible way neutral-coloured, transmission-reducing coating on glass can be obtained which also as a result of a toughening and/or bending process changed their optical properties only inconsiderably.

This problem is solved in accordance with the invention by the fact that the transmission-reducing coating is produced before the thermal toughening and/or bending process by means of a joint application of the metal or metal alloy from the elements with atomic numbers 22 to 28 and silicon as a metal silicide coating with a silicon content of at least 45 atom % by means of magnetron cathodic sputtering.

In connection with this, it can be arranged for the metal silicide coating to be applied by sputtering a silicon-containing metal alloy target.

Alternatively it can also be arranged for the metal silicide coating to be produced by co-sputtering of a metal or of a silicon-free metal alloy cathode and a silicon cathode.

A further form of embodiment of the invention proposes that a metal silicide coating of a composition $MeSi_n$, where "Me" means "Metal" where n =1 or 2 is applied. Such stoichiometric compositions give relatively homogeneous coatings which have properties which can be reproduced particularly well and are minimally susceptable to oxidation; coatings produced in accordance with this form of embodiment of the invention are also particularly resistant to corrosion and scratching.

In connection with this, it can also be arranged for a metal silicide coating of the composition $NiCrSi_2$, $FeSi_2$, $TiSi_2$, $CrSi_2$ or $CoSi_2$ to be applied.

Alternatively, it can also be arranged for a metal silicide coating of a composition NiSi and/or $NiSi_2$ is applied. This form of embodiment of the invention has a particular advantage that nickel silicide targets can be produced well from the powder metallurgy point of view.

Finally, the invention is characterised in a preferrred form of embodiment by the fact that the metal silicide coating is applied in a thickness of 5 to 80 nm. With the metal silicide coating in this thickness range, coatings are produced which lead to a reduction in transmission of 10 to 90% with appropriate adjustment of the coating thickness in particular also to a reduction in light transmission of the glass lights to approx. 40 to 60%. In this range, which is particularly attractive for automotive applications, de-reflection of the glass seen from the uncoated side is also achieved, whilst with greater coating thicknesses the reflection capacity of course increases again. A particular advantage of glass lights produced in accordance with the invention lies in this anti-reflection effect in the preferred light transmission range.

The invention is based upon the surprising finding that metal silicide coatings which are applied in the manner claimed on the one hand by magnetron cathodic sputtering or similar and on the other with the content claimed of silicon, virtually do not change their optical properties in transmission and reflection during the toughening or bending process. In particular, the view in transmission remains grey-neutral, whilst the light reflection capacity of the side of the glass facing away from the transmission-reducing coating normally is easily reduced somewhat. This process is surprising to the extent that, as already stated, it is known that pure transition metal coatings oxidise in the toughening process and thus completely change their optical properties, whilst pure silicon coatings for the most part withstand the toughening process unchanged, however have a very high reflection capacity. The magnetron cathodic sputtering process or a process which acts in an identical fashion is essential to the invention for producing the above coatings, as with this sufficiently high sputtering rates can be achieved which prevent the reaction of the metal or silicon with the residual gas found in normal high vacuum systems from leading to oxide formation. Otherwise, in particular with conventional cathodic sputtering, as for example applied in the process in accordance with DE-OS 21 38 034, the coatings are partly oxidised during the sputtering process, as a result of which the light transmission is too high, the view in transmission appears tinted and in addition the light reflection capacity rises sharply.

If the metal silicide coating in accordance with the invention is produced by co-sputtering of one or several metals with the atomic number 22 to 28 and a silicon target, care should be taken that the ratio of metal and silicon is correctly adjusted for example by choice of the sputtering rate. It is simpler from the process technology point of view to apply the metal silicide in the desired composition, on the basis of an alloy target, as in this case only one cathode with homogeneous material has to be controlled. The fact that a silicide alloy target cannot be produced with the same degree of purity as the initial materials is insignificant when using the material as a solar control coating, in contrast to semi-conductor electronics, in which the silicides are used as contact coatings.

The metal content of the silicide coating should for the rest not be much less than approximately 25 atom % in accordance with the invention, as undesirable optical properties in the silicon can appear with higher silicon contents. Apart from this, it lies within the concept of the invention that when carrying out the process in accordance with the invention coatings produced according to this should only cover part of the glass base, for example in the form of an anti-dazzle strip along one or more of the edges of automotive glass lights.

Further characteristics and advantages of the invention will become apparent from the description below, in which the invention is described in greater detail with reference to the drawing on the basis of examples of embodiment.

The following are shown:

Figure 1 The spectral transmission of glass lights produced in accordance with example I before (10) and after (12) thermal treatment at toughening temperature;

Figure 2 Spectral transmission of glass sheets produced in accordance with example II before (10) and after (12) thermal treatment at toughening temperature;

Figure 3 Spectral transmission of glass sheets produced in accordance with example III before (10) and after (12) thermal treatment at toughening temperature;

Figure 4 Spectral transmission of glass lights produced in accordance with example IV before (10) and after (12) thermal treatment at toughening temperatures; and

Figure 5 Spectral transmission of glass lights produced in accordance with example V before (10) and after (12) thermal treatment at toughening temperature, whereby in this case in addition the transmission curve (13) of a comparative glass light provided with a cobalt oxide coating is shown.

Example I

In a vacuum coating system, which was equipped with coating devices for magnetron cathodic sputtering, a coating with a light transmission of 60% was applied on to a float glass sheet measuring 10 x 10 cm^2 by means of simultaneous sputtering of a nickel target and a silicon target and a silicon target in an argon atmosphere at a pressure of 6 x 10^{-3} mbar. The sputtering rates were selected in such a way that the coating composition was approximately 30 atom % nickel and 70 atom % silicon. This was checked with the aid of auger electron spectroscopy. The coated sheet was then subjected to a toughening process. Following this, the coated sheet continued to have a greyish neutral view in transmission. The light transmission was 62% and the coating had a high degree of resistance to corrosion and scratching. Figure 1 shows that the thermal treatment at toughening temperature did not adversely change the neutral colour of the glass light and generally had only a slight effect upon the optical properties.

Example II

The process was carried out as in example I, however in place of the targets made of nickel and silicon, a target made of nickel silicide with a composition of 50.5% by weight Ni and 49.5 % by weight Si was used. With this target, a coating was applied in such a thickness that the coated glass light had a light transmission of 18.4%. As a result of toughening, the light transmission only increased to 20%. The properties of the coating were as in example I. Figure II shows that thermal treatment of the toughening temperature has not adversely changed the neutral colour of the glass light and generally has only had a slight effect upon the optical properties.

Example III

A metal silicon coating was applied as in example I. However, instead of the nickel target the cobalt target was used. The sputtering rates were set in such a way that the coating composition was approximately 45 atom % cobalt and 55 atom % silicon and the light transmission of the coated sheet was 54%.

After the toughening process, a light transmission of 55% was obtained with otherwise unchanged optical properties (figure 3).

Example IV

A coating with a light transmission of 35% was applied as in example I by the co-sputtering of the target made of chromium and a target made of silicon in a magnetron sputtering system. The sputtering rates were in this case chosen in such a way that the coating composition had approx. 60 atom % silicon and 40 atom % chromium.

Even in the case of a sheet coated in this way, no change in the optical properties was established after the toughening process (figure 4).

Example V
(comparative example:)

A coating with a light transmission of 32% was produced in a magnetron cathodic sputtering system, as described in example I, by means of the simultaneous sputtering of a cobalt target and a silicon target. The coating parameters were chosen in such a way that the coating had a composition of approximately 65 atom % cobalt and 35 atom % silicon. Curve 10 in figure 5 shows the spectral development in the transmission of this coating of 4 mm float glass before the toughening process. It does not differ greatly (apart from the level of transmission) from curve 10 in example III (figure 3). As a result of the toughening process, the light transmission increases to 39%. The view in transmission becomes highly umbral, and the reflection also has a yellowish brown colour cast.

This is also reflected in the spectral development of the transmission capacity, which is shown in curve 12 in figure 5. The reason for the colour cast lies in the proportion of cobalt in the coating being too high, which during the toughening process becomes cobalt oxide and causes the colour changes.

To demonstrate this, the spectral transmission capacity of a purely cobalt oxide coating is shown for comparison in curve 13 in figure 5. It shows the same characteristic structures which can also be found in curve 12. The characteristics of the invention disclosed in the above description and in the claims can be essential both individually as well as in any given combination for realising the invention in its various forms of embodiment.

List of Reference Numbers

10 Transmission curve (spectral) of a coated sheet before thermal treatment at toughening temperature

12 Transmission curve (spectral) of a coated sheet after thermal treatment at toughening temperature

13 Transmission curve of a sheet coated with a cobalt oxide coating for comparison.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Process for the manufacture of a toughened and/or bent sheet of soda-lime silica glass with reduced transmission, in particular solar control glass sheet, in which at least on one side of a transparent glass base at least one transmission-reducing coating with a considerable content of a metal or a metal alloy made of the elements with atomic numbers 22 to 28 in the periodic system is applied in such a thickness that the light transmission of the glass base provided with the transmission-reducing coating is between 10 and 90% of that of the glass base alone, and a thermal toughening and/or bending process is carried out in air at a temperature of 580°C to 680°C, preferably 600°C to 650°C, characterised by the fact that the transmission-reducing coating is produced by means of magnetron cathodic sputtering before the thermal toughening and/or bending process by the joint application of the metal or the metal alloy from the elements with atomic numbers 22 to 28 and silicon as a metal silicide coating with a silicon content of at least 45 atom %.

2. Process in accordance with claim 1, characterised by the fact that the metal silicide coating is applied by means of sputtering of a silicon-containing metal alloy target.

3. Process in accordance with claim 1, characterised by the fact that the metal silicide coating is produced by means of co-sputtering of a metal or a silicon-free metal alloy cathode and a silicon cathode.

4. Process in accordance with one of the previous claims, characterised by the fact that a metal silicide coating of a composition $MeSi_n$, where n =1 or 2, is applied.

5. Process in accordance with claim 4, characterised by the fact that a metal silicide coating of a composition $NiCrSi_2$, $FeSi_2$, $TiSi_2$, $CrSi_2$ or $CoSi_2$ is applied.

6. Process in accordance with claim 4, characterised by the fact that a metal silicide coating of a composition NiSi and/or $NiSi_2$ is applied.

7. Process in accordance with one of the previous claims, characterised by the fact that the metal silicide coating is applied in a thickness of 5 to 80 nm.

8. A process for the manufacture of a toughened and/or bent sheet of glass substantially as hereinbefore described with reference to the drawings and/or Examples.

~~9. The steps or features disclosed herein or any combination thereof.~~

Dated this 18th day of August 1987

FLACHGLAS AKTIENGESELLSCHAFT
By its Patent Attorneys
DAVIES & COLLISON

Fig.1

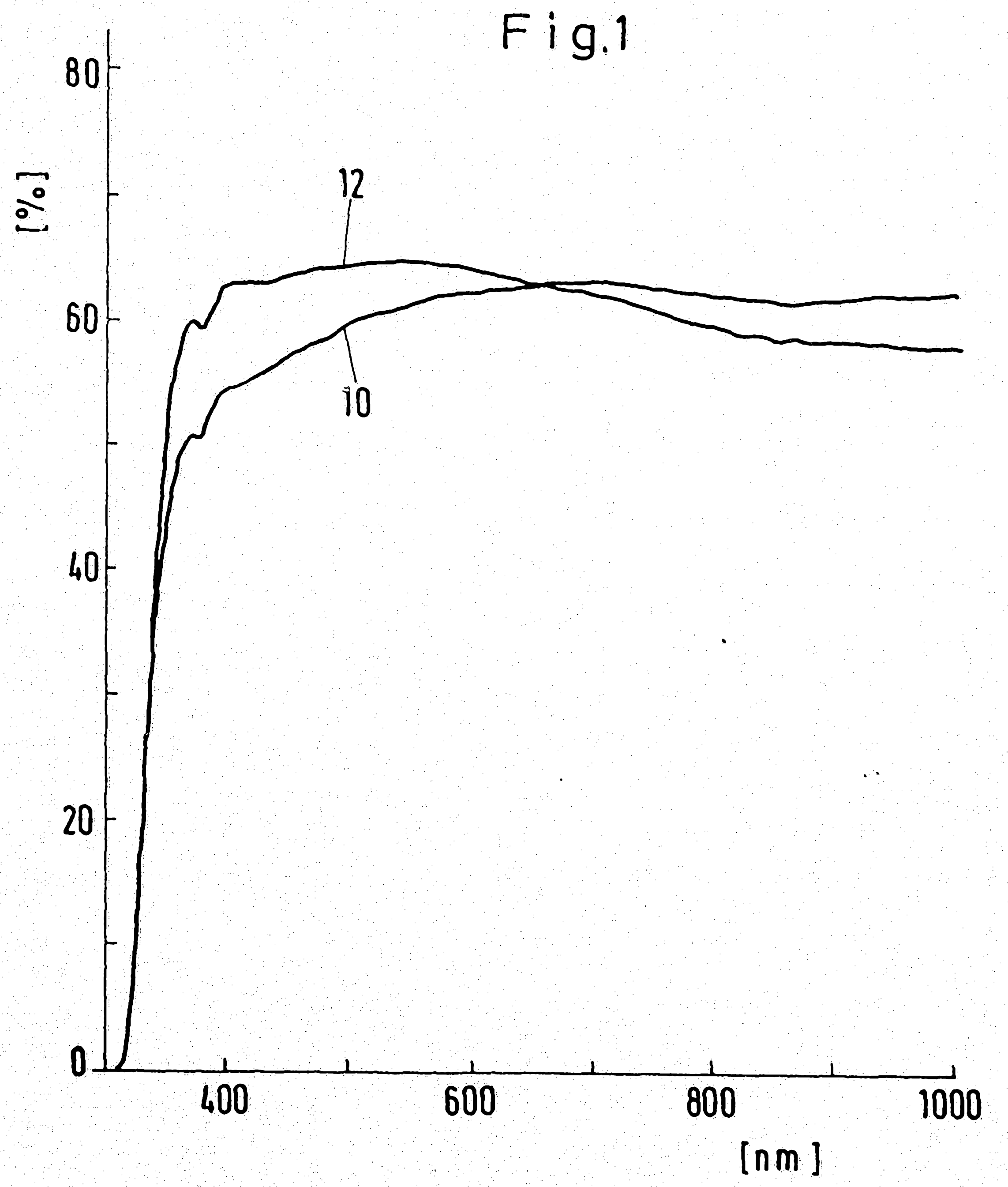

Fig.2

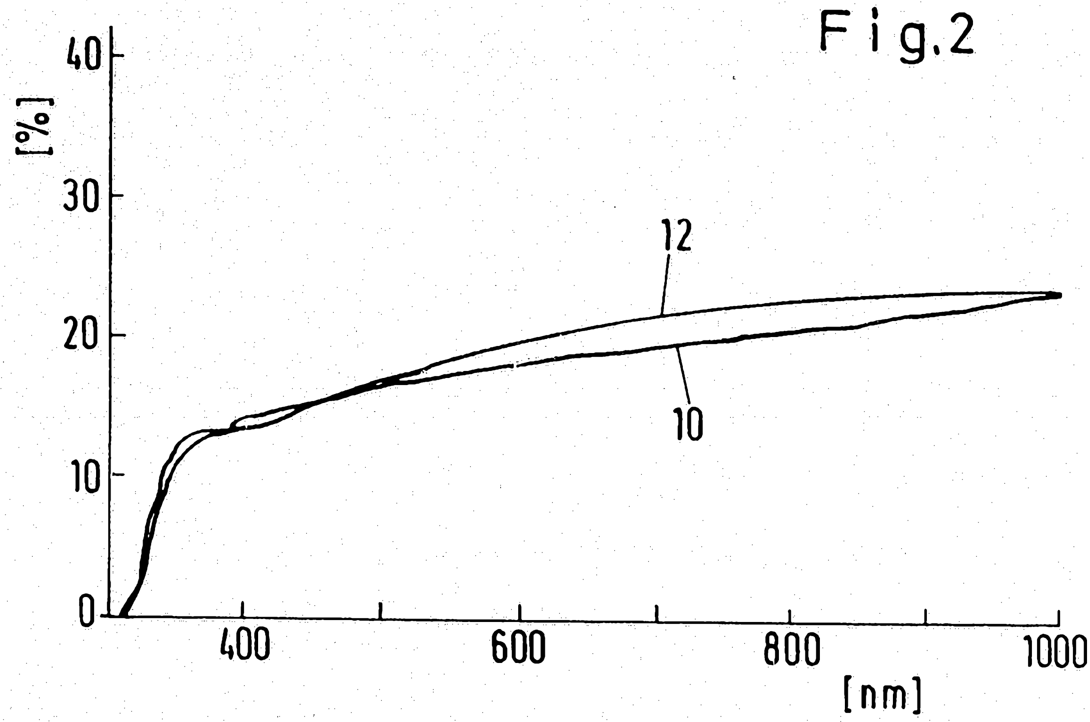

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Fig.4

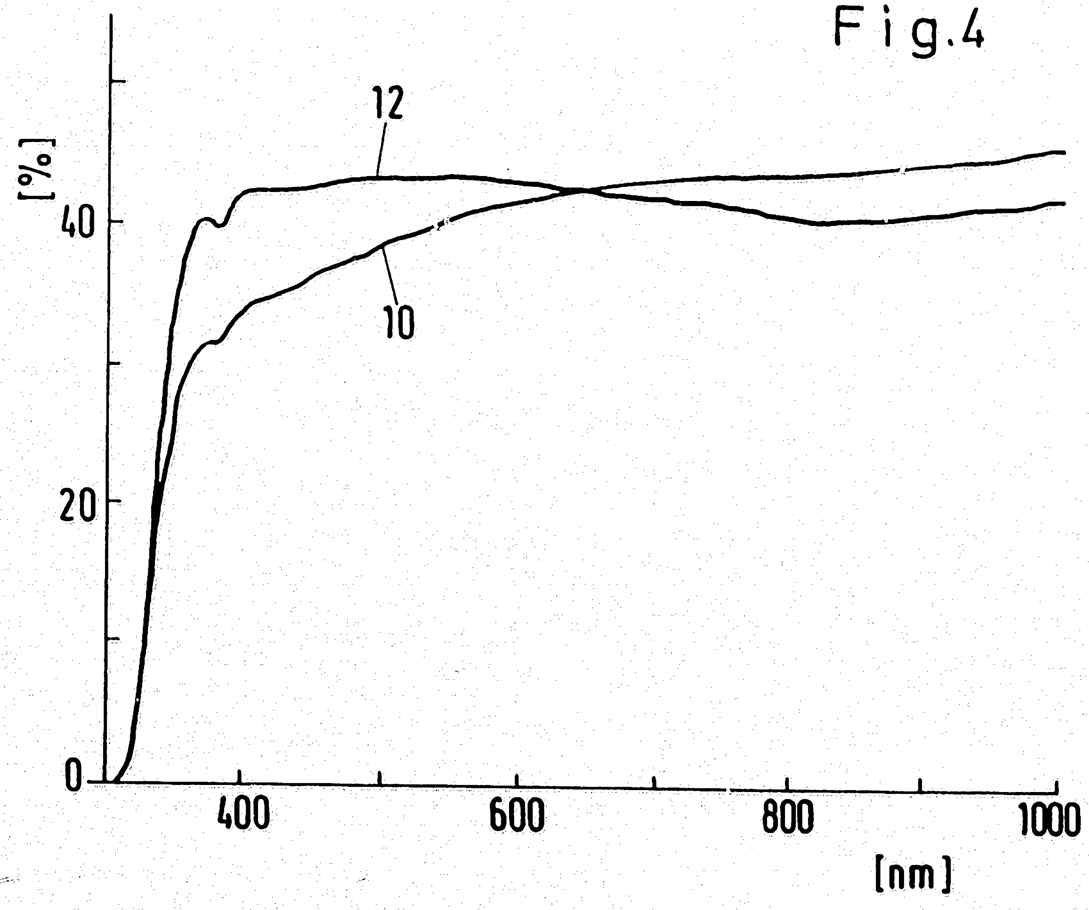

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Fig.3

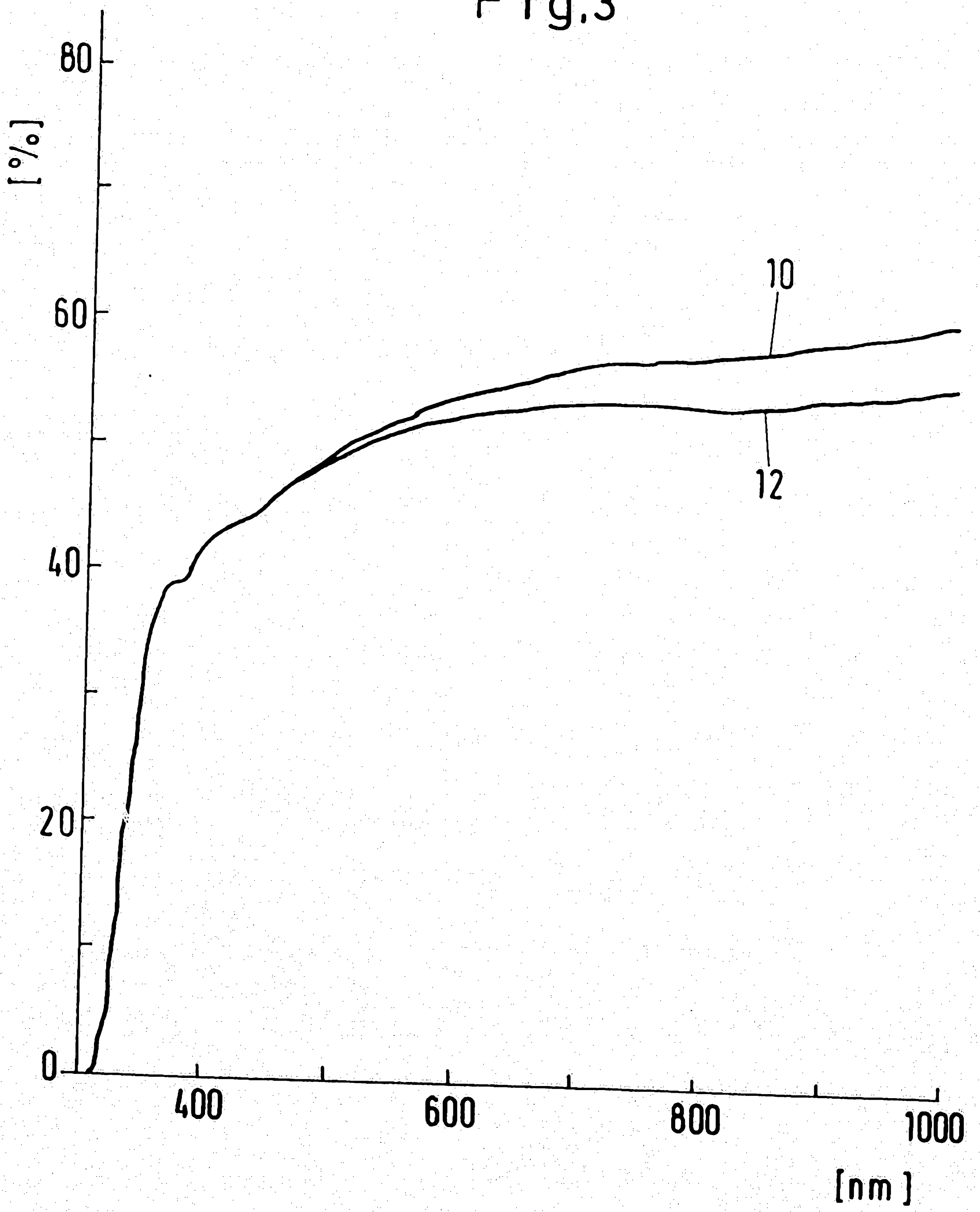

Fig.5