明 細 書

酸化チタン光触媒構造体及びその製造方法

技術分野

本発明は、優れた光触媒作用と光透過性を有し、特に透明性が要請される種々の構造物を構成する部材に光触媒作用を兼ね備えさせることを可能にした酸化チタン光触媒構造体及びその製造方法に関する。

背景技術

従来から光を照射すると物質の分解や酸化を促進する活性を示す光触媒が知られているが、最近この光触媒を利用して硫黄酸化物や窒素酸化物等の大気汚染物質を除去する試み等がなされており、その光触媒として酸化チタンを用いる試みもなされている（例えば、特開平６－３８５号公報、特開平６－４９６７７号公報、特開平６－３９２８５号公報等参照）。

ところで、近年、地球環境汚染に対する関心が高まっている中で、大気中のCO_2、NO_x及びSO_xなどの物質を除去する要請が高まり、また、これら有害物質を除去してアメニティー空間を創出する構想もみられているように、居住空間の脱臭・抗菌・防汚・防かび等への要請がますます強くなってきている。

そこで、このような汚染物質等を除去するために、上述の酸化チタン光触媒を利用することが考えられる。しかし、従来の酸化チタン光触媒は、一般に、処理すべき気体や液体等の被処理物を光触媒が収納された容器内に導入して光触媒に接触させ、同時に、外部から光を導入して光触媒に照射させるものであった。

また、この場合、光触媒に対する被処理物の接触面積の増大や光触媒に対する効率のよい光照射を行なうために、光触媒を微粒子状にしたり、あるいは、光触媒を透明基材に保持するようにした試み等もなされている。

しかしながら、上述の従来の酸化チタン光触媒においては、例えば、微粒子状に形成することによって被処理物との接触面積は増やせても、光を受ける実質面積についてはこれをそれ程増大させることはできないので、結局トータルの触媒効果を大きく向上させることは困難であった。

また、従来の酸化チタン光触媒はこれを例えばガラス基板等の上に薄膜状に形成する場合でも酸化チタン光触媒自体は透明性の低いものであった。これは、従来は、薄膜状に形成して実用レベルの光触媒作用を得るためには、酸化チタンゾルを基板上に焼結形成するか、あるいは、酸化チタンを微粉末にしてこれをバインダーで溶いて基板に塗布する以外に適当な方法がないと考えられていたためである。しかし、前者では高い活性を有しある程度の光透過性を有するものが得られるが、実用に耐える膜強度を得るためには焼結温度をガラス軟化点以上の温度に設定する必要がある為に少なくともガラス基板に形成するのは無理なものであった。しかも、光透過性については、いわゆる白濁傾向を示すもので、透明性が得られる程に可視光を通過させることは困難であり、この意味では不透明に近いものであった。また、後者の場合には、高温での焼結等の工程は不要であるが、微粉末化した酸化チタンを塗布するために白濁化して不透明なものであった。

さらに、この種の分野で従来からよく知られているゾルゲル法やＣＶＤ法等によって薄膜状にした酸化チタンでは透明性は確保できるが、実用レベルの光触媒活性を得られていない。

このように、従来の酸化チタン光触媒は、実用レベルの光触媒活性を示すものはいずれも実質的には不透明なものであったので、例えば、この従来の光触媒を透明ガラス基板等の表面に形成しても、このガラス基板の裏面側から照射した光を光触媒の表面部に有効に到達させることができないので、結局、利用できる光は、光触媒が形成された表面側から照射されたものだけとなる。したがって、この光触媒を、例えば、窓ガラスの表面に形成して室内の清浄化を行う場合には、当然、光触媒をガラスの室内に面した表面に形成することになる。そうすると、光触媒活性に利用できるのは室内側から照射

される光だけとなり、太陽光は利用できないことになるという重大な欠点が生じてしまう。

このように、従来の酸化チタン光触媒では、光触媒作用を行なう酸化チタン自体が実質的に不透明なものであることから、その触媒作用の向上に一定の限界が生じていたと共にその応用範囲も著しく限定されたものであった。

本発明は、上述の背景のもとでなされたものであり、優れた光触媒作用と光透過性を有し、しかも、特に透明性が要請される種々の構造物を構成する部材に光触媒作用を兼ね備えさせることを可能にした酸化チタン光触媒構造体及びその製造方法を提供することを目的としたものである。

発明の開示

上述の課題を解決するために本発明にかかる酸化チタン光触媒構造体は、

（構成１） 透光性基体上に、少なくとも、光触媒活性を有すると同時に波長５５０ｎｍの光に対する光直線透過率が５０％以上有する酸化チタン薄膜を形成してなる構成とし、

この構成１の態様として、

（構成２） 前記酸化チタン薄膜の膜厚が０．１μｍ～５μｍであることを特徴とする構成とし、

構成１又は２の態様として、

（構成３） 前記酸化チタン薄膜は少なくともアナターゼ結晶を含むものであることを特徴とする構成とし、

構成１ないし３のいずれかの態様として、

（構成４） 前記透光性基体と酸化チタン薄膜との間に光透過性を有するプレコート薄膜を設けたことを特徴とする構成とし、

この構成４の態様として、

（構成５） 前記プレコート薄膜の膜厚が０．０２～０．２μｍであることを特徴とする構成とし、

構成１ないし５のいずれかの態様として、

（構成６）　前記透光性基体がガラスであることを特徴とする構成とし、構成４ないし６のいずれかの態様として、

（構成７）　前記プレコート薄膜がSiO_2を主成分とする材料からなることを特徴とする構成とした。

また、本発明にかかる酸化チタン光触媒構造体の製造方法は、

（構成８）　透光性基体の上に酸化チタン薄膜をパイロゾル法、ディップ法、印刷法又はＣＶＤ法によって成膜する工程を含む製造工程によって構成１ないし７の酸化チタン光触媒構造体を製造することを特徴とする構成としたものである。

上述の構成１によれば、酸化チタン光触媒構造体を、透光性基体上に少なくとも光触媒活性を有すると同時に波長５５０ｎｍの光に対する光直線透過率が５０％以上有する酸化チタン薄膜を形成して構成したことにより、優れた光触媒作用と光透過性を有し、しかも、特に透明性が要請される種々の構造物を構成する部材として用いることができる酸化チタン光触媒構造体を得ることが可能になった。

これは、酸化チタン薄膜を波長５５０ｎｍの光に対する光直線透過率が５０％以上有するものとしたことにより、光触媒活性作用を得るために必要な光照射効率を実質的に増大させることが容易に可能になり、同時に、可視光に対する透明性も確保できるようになったためである。すなわち、酸化チタン薄膜を波長５５０ｎｍの光に対する光直線透過率が５０％以上有するものにすると、必然的に、光触媒活性作用を得る光（波長約４００ｎｍ）に対する透過性も表裏からの照射光を有効に利用できる程度に備えることになる。したがって、この酸化チタン光触媒構造体の両側から別個の光を照射すると、外部に接する側の酸化チタン薄膜表面部には、この両側からの光が加算されて達する。つまり、酸化チタン薄膜表面部に対する光照射効率を実質的に増大させることができる。これにより、酸化チタン薄膜表面部における光触媒活性がこれに対応して増大し、優れた光触媒作用を得ることが可能になる。同時に、酸化チタン薄膜を波長５５０ｎｍの光に対する光直線透過率が５０

％以上有するようにしたことにより必然的に可視光に対する十分な透明性も確保できる。これにより、特に透明性が要請される種々の構造物、例えば、ガラス窓等を構成する部材としてこの酸化チタン光触媒構造体を用いることができることになり、例えば、室内の炭酸ガスや大気汚染物質（ＮＯx やＳＯx など）の除去、脱臭・抗菌・防汚・防かび等の作用を特別な装置を用いることなく窓ガラス自体によって行なわせるという画期的な効果を得ることが可能になる。しかも、窓ガラスに適用して室内の清浄化を行う場合には、太陽光を極めて有効に利用できるという大きなメリットが得られる。さらに、特に、近年多くみられるガラス材を多用したビル建築物等に適用すれば、その居住空間の清浄化に対する効果ははかりしれないものとなる。また、その他にも、例えば、かびや腐蝕を極力嫌うカメラ等の精密機器その他を保管するためのガラス戸等を備えた保管棚のガラス戸等にも用いることができ、その応用範囲は極めて広い。　構成２によれば、酸化チタン薄膜の膜厚を０．１μｍ～５μｍにすることによって、十分な光触媒活性を有し同時に波長５５０ｎｍの光に対する光直線透過率が５０％以上有する酸化チタン薄膜が得られる。膜厚を０．１μｍ未満にすると十分な光触媒活性が得られなくなる。また、膜厚を５μｍを越えたものにすると、波長５５０ｎｍの光に対する光直線透過率が５０％未満になって十分な透明性を確保できなくなる。

構成３によれば、酸化チタン薄膜をアナターゼ結晶が含まれるものとすることにより、より光触媒活性の優れたものとすることができる。

構成４によれば、透光性基体と酸化チタン薄膜との間に光透過性を有するプレコート薄膜を設けることにより、透光性基体の物質が酸化チタン薄膜に浸透する等により酸化チタン薄膜の光触媒作用が劣化する等の弊害を防止でき、また、これにより、透光性基体の材質の選択の幅を拡げることが可能となり、さらには、透光性基体に直接酸化チタン薄膜を形成する場合には、透光性基体の物質が酸化チタン薄膜に浸透してもそれが電荷分離作用を行う酸化チタンには至らない程度に酸化チタンの膜厚を厚くする必要があったが、その必要がなくなったことで、透光性基体の材質如何にかかわらず酸化チタ

ン薄膜の膜厚を著しく薄くしても十分な光触媒作用が得ることが可能になった。この点は、光照射効率の本質的向上及び透明性向上の観点から重大な意味を持つ。

プレコート薄膜の膜厚は、構成５のように、０．０２～０．２μｍであれば、プレコート薄膜として採用可能な物質一般を考慮した場合でも、十分な透明性を確保した上で物質の浸透を阻止する効果を得ることができる。逆に、０．０２μｍ未満では十分な物質浸透阻止効果を得ることが困難になり、０．２μｍを越えた膜を形成しても物質浸透阻止効果にはそれ以上有利な点は生じないばかりでなく、成膜操作が煩雑になると共に、材料によっては透明性を確保できなくなる場合があるからである。

透明基体として、構成６のように、ガラスを用いれば、既に説明した通り極めて広い応用が可能になる。この場合には、構成７のように、プレコート薄膜をSiO_2で構成すれば、最良の透明性及び物質浸透阻止性を確保できる。

さらに、構成８の方法によれば、構成１ないし７の酸化チタン光触媒構造体を比較的容易に得ることが可能になる。

図面の簡単な説明

第１図は、実施例１にかかる酸化チタン光触媒構造体の部分断面図であり、第２図は、実施例７にかかる酸化チタン光触媒構造体の部分断面図であり、第３図は、実施例及び比較例の各薄膜の膜厚並びに光触媒活性測定結果及び光直線透過率測定結果を表にして掲げた図面であり、第４図は、実施例１６ないし１８の油脂分解活性の測定結果をグラフにして示した図であり、第５図は、実施例１９及び２０の油脂分解活性の測定結果をグラフにして示した図である。

発明を実施するための最良の形態

（実施例１）

図１は本発明の実施例１にかかる酸化チタン光触媒構造体の部分断面図である。以下、図１を参照にしながら実施例１の酸化チタン光触媒構造体及びその製造方法を説明する。

図１において、この実施例の酸化チタン光触媒構造体は、透光性基体１の上に酸化チタン薄膜２を形成したものである。

透光性基体１は、厚さ１ｍｍ、縦100ｍｍ、横５０ｍｍのソーダライムガラス基板である。

酸化チタン薄膜２は、アナターゼ結晶を含む膜厚４．８μｍの酸化チタン薄膜である。

上記酸化チタン光触媒構造体は次のようにして製造した。

まず、厚さ１ｍｍのソーダライムガラスを、縦１００ｍｍ、横５０ｍｍに切り出して、透光性基体１を作製した。

次に、酸化チタン膜の原料として、チタンイソプロポオキシドをアセチルアセトン溶媒に溶かして、チタンイソプロポオキシドの濃度を０．５ｍｏｌ／Ｌに調整した原料溶液を作製した。

次に、パイロゾル成膜装置に上記透光性基体１セットし、該透光性基体１を５００℃に加熱しておき、上記原料溶液を超音波により霧化させて２０ｍＬ／ｍｉｎで上記透光性基体１の表面に導入して約６０分間成膜することにより、透光性基体１の上に膜厚４．８μｍの酸化チタン薄膜２が形成された酸化チタン光触媒構造体を得た。なお、この酸化チタン薄膜２を薄膜Ｘ線回折分析で観測したところ、アナターゼ結晶を含むものであることが確認できた。

次に、得られた酸化チタン光触媒構造体の触媒活性及び光直線透過率を以下の方法で測定した。

光触媒活性測定法

酸化チタン光触媒構造体を、１．５Ｌの円筒形のガラス密閉容器内の底に酸化チタン薄膜２が上方を向くようにして載置し、この容器内にアセトアルデヒドを濃度が１３００ｐｐｍになるように導入した。次に、上記酸化チタ

ン光触媒構造体に１０Ｗのブラックライト３本を用いて酸化チタン薄膜２の表面の上方から光を照射した。このときの酸化チタン薄膜２の表面における照度は１．２ｍＷ／ｃｍ^{2}であった。しかる後に、ＦＩＤ付きガスクロマトグラフにより上記ガラス密閉容器内のアセトアルデヒドの定量分析を行い、光照射後におけるアセトアルデヒドの減少量を求め、その減少量を触媒活性の度合いとした。

光直線透過率の測定法

光直線透過率測定器（株式会社島津製作所製のＵＶ－３１００ＰＣ）に実施例１の酸化チタン光触媒構造体をセットし、５５０ｎｍの波長における光の直線透過率を測定した。

上述の方法による測定結果は、分解活性が１０．５μｌ／min、光透過率が７０％であり、優れた光触媒活性と十分な透明性を有することが確認できた。

また、上記酸化チタン光触媒構造体を裏返しにして、すなわち、上記円筒形のガラス密閉容器内の底に酸化チタン薄膜２が対向するようにして載置し、上記同様の方向、すなわち、透光性基体１の酸化チタン薄膜２が形成されていない側から光を照射して光触媒活性を測定したところ、上記の場合とほぼ同じ光触媒活性作用が得られることが確認された。この結果は、透光性基体１の裏面から照射された光も表側から照射した光と同等に酸化チタン薄膜２の光触媒活性に寄与することを示しており、両側から光を照射すれば、その光触媒効果を著しく増大させることが可能であることを示している。

（実施例２～６）

これらの実施例は、実施例１における酸化チタン薄膜２の膜厚を異ならしめたほかは実施例１と同様の構成を有し同様の製造方法で製造したものであるので、各実施例の膜厚、並びに、光触媒活性測定結果及び光直線透過率測定結果を、図３に表にして掲げてその詳細説明は省略する。

図３の表に示されるように、各実施例とも優れた光触媒活性と十分な透明性を有することがわかる。

（実施例７～１２）

これらの実施例は、図２に示したように、実施例１における酸化チタン薄膜２と透光性基体１との間に、SiO_2 薄膜からなるプレコート薄膜３をデップコートによって形成したほかは実施例１と同様の構成を有し同様の製造方法で製造したものであるので、各実施例の膜厚、並びに、光触媒活性測定結果及び光直線透過率測定結果を、図３に表にして掲げてその詳細説明は省略する。

図３の表に示されるように、プレコート薄膜３がない実施例１～６に比較して、酸化チタン薄膜２の膜厚を薄くしても優れた光触媒活性を示すことから、より高い透明性を確保できることがわかる。

（実施例１３～１４）

これらの実施例は、実施例１における透光性基体１のソーダライムガラスを石英ガラスに代えたほかは実施例１と同様の構成を有し同様の製造方法で製造したものであるので、各実施例の膜厚、並びに、光触媒活性測定結果及び光直線透過率測定結果を、図３に表にして掲げてその詳細説明は省略する。

図３の表に示されるように、透光性基体１を石英ガラスにしたことから、プレコート薄膜３がなくても優れた光触媒活性を示し、同時に、十分な透明性を有することがわかる。

（実施例１５）

この実施例は、実施例１における酸化チタン薄膜の成膜時における温度を３８０℃に変え、また、成膜後に空気雰囲気下で４００℃で６０分間熱処理する工程を追加したほかは実施例１と同様の構成を有し同様の製造方法で製造したものであるので、この実施例の膜厚、並びに、光触媒活性測定結果及び光直線透過率測定結果を、図３に表にして掲げてその詳細説明は省略する。

図３の表に示されるように、この実施例も優れた光触媒活性と十分な透明性を有することがわかる。

（実施例１６）

この実施例は、透光性基体１上に、厚さ０．０６μｍのSiO_2 膜からな

るプレコート薄膜３を形成し、その上に、厚さ０．８μｍの酸化チタン薄膜２をいわゆるディップ法によって形成した例である。

透光性基体１として、厚さ１ｍｍ、縦１００ｍｍ、横５０ｍｍのソーダライムガラス製の板を使用した。この透光性基体１をシリコンアルコキシドの溶液（日本曹達（株）製：商品名アトロンＮＳｉ－５００）８００ｍｌをいれた幅１００ｍｍ、奥行き５０ｍｍ、高さ２００ｍｍの容器にゆっくりと浸漬し、１０ｃｍ／ｍｉｎの速度でゆっくりと引き上げた。これを１５０℃で乾燥後、５００℃で１時間焼成して透光性基体１上に膜厚０．０６μｍのSiO_2薄膜を形成させてプレコート薄膜３とした。

次に、チタニウムテトライソプロポキシドを有機溶剤と反応させて得られるディップ用有機チタン溶液（日本曹達（株）製：商品名アトロンＮＴｉ－５００）８００ｍｌの中に、プレコート薄膜を設けたガラス基板をゆっくりと浸漬して、１０ｃｍ／ｍｉｎでゆっくりと引き上げた。１２０℃で乾燥後、５００℃で１時間焼成して、プレコート薄膜上に酸化チタン薄膜を形成させた。この酸化チタン薄膜形成用の薬液への浸漬と乾燥・焼成を１０回繰り返して酸化チタン薄膜の膜厚を０．８μｍにし、本実施例の酸化チタン光触媒構造体を得た。

こうして得られた酸化チタン光触媒構造体の５５０ｎｍの波長の光に対する光直線透過率は８１％であった。また、この実施例については、光触媒活性の１つとして油脂分解活性を取り上げ、次のようにして評価した。

油脂分解活性の評価

上記酸化チタン光触媒構造体を、縦５０ｍｍ×横５０ｍｍの大きさの試料片に切り出し、その表面を市販のサラダ油を染み込ませたティッシュペーパーで軽く全面をふいて、０．１ｍｇ／ｃｍ^{2}のサラダ油塗布量になるように塗布・拭き取りによって調整した。サラダ油の初期塗布量はガラス板を０．１ｍｇの秤量精度を有する精密天秤で秤量して測定した。この塗布済み基板に紫外線強度計（ウルトラバイオレット社製）で紫外線強度３ｍＷ／ｃｍ^{2}になるように紫外線ランプ（松下電工株式会社製１０Ｗブラックライト ＦＬ

１０ＢＬＢを３本並べて照射）と試料片表面との間隔を調節して、所定時間後の重量を測定してサラダ油（油脂）の分解量を求めた。

図４に実施例１６の光触媒構造体の油脂分解特性をグラフにして示した。なお、図４のグラフにおいては、縦軸が油脂残存率（単位；％）、横軸が紫外線照射時間（単位；時間）である。また、酸化チタン薄膜を形成していないプレコート薄膜のみを設けたガラス基板の上に、上記と同様にサラダ油を塗布して紫外線（上記ブラックライト）を照射し、所定時間後の重量変化を測定してブランク試料とした。その結果も合わせて図４のグラフに示した。図４から明らかなように、この酸化チタン光触媒構造体は、勝れた油脂分解活性を有していることがわかる。

（実施例１７）

この実施例は、透光性基体１上に、厚さ０．０６μｍのSiO_2膜からなるプレコート薄膜３を形成し、その上に、厚さ０．６μｍの酸化チタン薄膜２を、いわゆるスプレー法によって形成した例である。

実施例１６と同様にして、厚さ１ｍｍ、縦１００ｍｍ、横５０ｍｍのソーダライムガラス製の板を使用して、膜厚０．０６μｍのSiO_2薄膜を形成させプレコート薄膜３とした。

次に、このプレコート薄膜３を形成した透光性基体１を、５００℃に加熱した箱型ヒーターの奥にたてかけて、チタニウムテトライソプロポキシド１４０ｇとアセチルアセトン２００ｇとを反応させて得られるチタニウムアセチルアセトナートの有機溶剤溶液を、噴霧器を使用して、前記プレコート薄膜３を形成した透光性基体１のプレコート薄膜３上に１０ショットスプレーし、熱分解させて、膜厚０．６μｍの酸化チタン薄膜２を形成させた。

こうして得られた酸化チタン光触媒構造体の、波長５５０ｎｍの光に対する光直線透過率は７８％であった。光触媒活性としての油脂分解活性を実施例１６と同様にして測定し、図４に実施例１６の結果とともに示した。

（実施例１８）

この実施例は、透光性基体１上に、厚さ０．０６μｍのSiO_2膜からな

るプレコート薄膜３を形成し、その上に、厚さ０．４μｍの酸化チタン薄膜２をいわゆる印刷法によって形成した例である。

実施例１６と同様にして、厚さ１ｍｍ、縦１００ｍｍ、横５０ｍｍのソーダライムガラス製の板を透光性基体１として使用し、この上に厚さ０．０６μｍのプレコート薄膜３を形成させた。

次に、チタニウムテトライソプロポキシド７０ｇ、エチルセルロース１０ｇ、有機溶剤１２００ｇを反応溶解させて得られる薬液を、４００メッシュのスクリーンを備えた印刷機により前記プレコート薄膜３の上にスクリーン印刷した。印刷後、５分間静置してレベリング後、５００℃に加熱した電気炉中にいれて焼成した。この印刷・焼成を５回繰り返して膜厚０．４μｍの酸化チタン薄膜２を形成させ、酸化チタン光触媒構造体とした。

この構造体の波長５５０ｎｍの光に対する光直線透過率８６％であった。また、この薄膜について、実施例１６と同様に油脂分解活性を測定したところ、図４にグラフにして示した結果が得られた。

（実施例１９）

この実施例は、透光性基体１上に、厚さ０．０４μｍのSiO_2膜からなるプレコート薄膜３をパイロゾル法によって形成し、その上に、厚さ０．４μｍの酸化チタン薄膜２をディップ法によって形成した例である。

厚さ１ｍｍ、縦１００ｍｍ、横５０ｍｍのソーダライムガラスからなる基板をパイロゾル成膜装置にセットし、有機シリコン溶液（日本曹達（株）製：商品名アトロンＮＳｉ－５００）を超音波により霧化させて、２０ｍｌ／ｍｉｎの速度で５００℃に加熱したガラス基板に２分間導入し酸化珪素からなる膜厚０．０４μｍのプレコート薄膜３を形成させた。

次にこのプレコート薄膜３の上に実施例１６と同様にしてディップ法により酸化チタン薄膜を形成させた。ディップ、浸漬、乾燥、焼成を５回繰り返すことにより、膜厚０．４μｍの透明な酸化チタン薄膜２が形成された酸化チタン光触媒構造体が得られた。

この酸化チタン光触媒構造体の波長５５０ｎｍの光に対する光直線透過率

は８９％であった。また、この光触媒構造体の油脂分解活性を測定したところ、図５にグラフにして示した結果が得られた。

（実施例２０）

この実施例は、透光性基体１上に、厚さ０．０６μｍのSiO_2膜からなるプレコート薄膜３を形成し、その上に、厚さ０．６μｍの酸化チタン薄膜２をいわゆるＣＶＤ成膜法によって形成した例である。

厚さ１ｍｍ、縦１００ｍｍ、横５０ｍｍのソーダライムガラスからなる基板を透光性基体１として、この上に実施例１６と同一の方法により酸化珪素からなる膜厚０．０６μｍのプレコート薄膜３を形成させた。

次に、このプレコート薄膜３を形成させた透光性基体１を常圧ＣＶＤ成膜装置にセットし、チタニウムテトライソプロポキシドを２００℃に加熱した気化器に仕込み、窒素ガスを５０ｍｌ／ｍｉｎの流量で気化器へ導入してバブリングさせ、加熱した導管を通してチタニウムアルコキシドの蒸気をガラス板を設置した成膜部へ導入した。成膜部は５００℃に加熱し、空気２００ｍｌ／ｍｉｎを一緒に導入し５分間成膜することにより、プレコート薄膜３の上に膜厚０．６μｍの酸化チタン薄膜２を形成させて酸化チタン光触媒構造体とした。

この酸化チタン光触媒構造体の波長５５０ｎｍの光に対する光直線透過率は８４％であった。また、この光触媒構造体の油脂分解活性を測定したところ、図５にグラフにして示した結果が得られた。

（比較例１）

この比較例は、実施例１における酸化チタン薄膜２の膜厚を０．０５μｍと薄くしたほかは実施例１と同様の構成を有し同様の製造方法で製造したものであるので、この比較例の膜厚、並びに、光触媒活性測定結果及び光直線透過率測定結果を、図３に表にして掲げてその詳細説明は省略する。

図３の表に示されるように、この比較例では、透明性はよいが、ほとんど光触媒活性を示さないことがわかる。

（比較例２）

この比較例は、実施例１における酸化チタン薄膜２の成膜際の温度を３８０℃に変えたほかは実施例１と同様の構成を有し同様の製造方法で製造したものであるので、この比較例の膜厚、並びに、光触媒活性測定結果及び光直線透過率測定結果を、図３に表にして掲げてその詳細説明は省略する。なお、こうして製造した酸化チタン光触媒構造体の場合、酸化チタン薄膜２にアナターゼ結晶が全く含まれていないことが薄膜Ｘ線回折分析によって確認されている。

図３の表に示されるように、この比較例では、透明性は十分であるが、ほとんど光触媒活性を示さないことがわかる。

（比較例３）

この比較例は、実施例１における酸化チタン薄膜２の成膜を、パイロゾル法ではなく、酸化チタン粉末（日本アエロジル社製のＰ－２５）０．１ｇを水に分散させたものを塗布するという方法を用いて成膜したほかは実施例１と同様の構成を有し同様の製造方法で製造したものであるので、この比較例の膜厚、並びに、光触媒活性測定結果及び光直線透過率測定結果を、図３に表にして掲げてその詳細説明は省略する。

図３の表に示されるように、この比較例では、光触媒活性は高いが、透明性がほとんどないことがわかる。

なお、本発明に使用する透光性基体は、光学的に所定の透光性を有していれば特に制限は無く、具体的には、パイレックス硝子、石英硝子、鉛硝子、ソーダライム硝子などがある。実用的な面から安価なソーダライムガラスが主に用いられる。ガラス基板中のナトリウムなどアルカリ成分を含まない石英ガラスやナトリウムなどアルカリ成分の少ないボロシリケートガラスなども好適に用いられる。　酸化チタン薄膜の光触媒活性は、透光性基体がソーダライムガラスなどの場合、基体から拡散してくるナトリウムなどのアルカリ成分により阻害されるので、該拡散防止のために、透光性基体上にプレコート膜を設けることが好ましい。この場合、安価なソーダライム硝子等のアルカリ成分が拡散する恐れのある透光性基体を使用した場合においても有利

に使用できる。

酸化チタン膜は、厚さ０．１μｍ～５μｍであり、０．１μｍ以下であると透明感はあるが光活性が低く実用性がなくなり、５μｍを越えると光触媒活性を高く維持でき、光干渉による着色も減少するなど利点もあるが、白濁斜向となり、また膜剥離や成膜に長時間かかるなどの欠点も発生する傾向がある。

また、成膜する酸化チタンの膜厚を大きく例えば０．３μｍ～５．０μｍとし、酸化チタン薄膜中のナトリウム濃度を傾斜的に低下させ、薄膜表面近傍においての酸化チタンを光触媒として活用する事も可能であり、この場合、プレコート薄膜を省略することができる。

プレコート薄膜は、厚さ０．０２μｍ～０．２μｍであり、０．０２μｍ以下であるとアルカリ拡散防止能が低くなり、０．２μｍ以上ではアルカリ拡散防止能の観点からは支障はないが、光透過性が低下し、又、成膜操作が煩雑となるので好ましくない。プレコート薄膜により、基板からのナトリウムなどのアルカリ成分の拡散を防止するため、酸化チタン薄膜を薄くすることが可能となり、より可視光領域で透明度の高い酸化チタン薄膜を形成することを可能になる。

プレコート膜の組成は、可視光透過率が高く、基板からのナトリウムの拡散を押さえる事が可能な薄膜なら制限はなく、たとえば、酸化硅素薄膜、酸化錫薄膜、インジュームドープ酸化錫薄膜、酸化インジューム薄膜、錫ドープ酸化インジューム薄膜、酸化ゲルマニューム薄膜、酸化アルミナ薄膜、酸化ジルコニューム薄膜、$SiO_2 + MO_X$（MO_X はP_2O_5、B_2O_3、ZrO_2、TiO_2、Ta_2O_5 からなる群より選ばれた少なくとも一種の金属酸化物）薄膜をその例としてあげることが出来るが、アルカリ拡散防止能の見地から、酸化硅素薄膜又はSiO_2 にP_2O_5 を５重量％程度添加した薄膜が特に好ましい。

さらに、光触媒活性の高い酸化チタン薄膜を得るための必要条件は、少なくともアナターゼ結晶を含むことが必要である。アナターゼ結晶は、成膜温

度または成膜後の熱処理温度が高いと相転移して一部がルチル結晶に変化するのでルチル結晶を含んだアナターゼ結晶の酸化チタン薄膜も好適に用いられる。しかし、高温でアナターゼの結晶のすべてをルチル結晶にすると相転移による酸化チタンの白濁が生じるので可視光透過率を減少させるため好ましくない。

本発明において、成膜法としてはパイロゾル法が最適であるが、プレコート薄膜及び酸化チタン薄膜とも一般的に知られている成膜法も採用することは可能である。すなわち、スパッタ法、電子ビーム蒸着法、イオンプレーティング法、化学気相成膜法（ＣＶＤ法）、スプレー法、ディップ法等でもその成膜制御を工夫すれば本発明に適用することは可能である。なお、パイロゾル法やスプレー法のように常圧でミストを吹き付けて成膜する方法は、実際の工業生産を考えた場合、例えば、板ガラス製造中のガラス冷却時にガラス板がまだ熱い状態でミストを吹き付けるという適用の仕方ができるので好ましい。ただし、基板を硝子軟化点以上の高温例えば６００℃以上の高温に保つ必要のある成膜法は、基板の変形や基板からのナトリウムなどのアルカリ成分の拡散を促進する為、好ましくない。

成膜法としては、いわゆるパイロゾル法は、高純度で安価なチタンアルコキシドを原料にして、成膜速度が早くかつアナターゼ結晶性を含む、高活性の酸化チタン薄膜が高均一、大面積で得ることが出来、４００℃～５５０℃程度のガラス軟化点以下の温度で成膜が可能で、このレベルの温度であればナトリウムなどの拡散の程度を押え、また、プレコート層でそれらのブロックも十分可能な温度であるため、好ましい。パイロゾル法とは、常圧化学蒸気分解法（ＣＶＤ法）の一種であり、超音波によりアトマイズされたミストを４００℃～５５０℃で加熱された基板上に気相輸送し、基板上で熱分解して得られる方法により、プレコート膜或いは酸化チタン薄膜を成膜する。

プレコート膜を製造する薬剤としては、SiO_2 を生成するものとしては、$Si(OCH_3)_4$,$Si(OC_2H_5)_4$,$SiCH_3(OCH_3)_3$ などのシリコンアルコキシドおよびその縮合物や$SiCl_4$ などのシリコンハロゲン化物などがあり、酸

化錫を生成するものとして、$Sn(OCH_3)_4$, $Sn(OC_2H_5)_4$, $Sn(OC_4H_9)_4$, $Sn(AcAc)_4$, $Sn(OCOC_4H_{15})_4$, $SnCl_4$ などがあり、酸化インジュームを生成するものとして、$In(OCH_3)_3$, $In(OC_2H_5)_3$, $InCl_3$, $In(AcAc)_3$, $In(NO)_3nH_{20}$ などがあり、酸化ゲルマニュームを生成するものとしては、$Ge(OC_2H_5)_4$, $Ge(OC_4H_9)_4$, $GeCl_4$ などがあり、酸化アルミナを生成するものとしては、$Al(OC_2H_5)_3$, $Al(iOC_3H_7)_3$, $Al(OC_4H_9)_3$, $Al(AcAc)_3$, $Al(NO_3)_{39}H_{20}$ などがあり、五酸化リンを生成するものとして、$P(OC_2H_5)_3$, $PO(OCH_3)_3$, $PO(OC_2H_5)_3$, H_3PO_4, P_2O_5などがあり、酸化ホウ素を生成するものとしては、$B(OCH_3)_3$, $B(OC_2H_5)_3$, $B(OC_4H_9)_3$, $B(AcAc)_3$, BC_{13}, H_3BO_3 などがあり、これら通常使用可能なものが使用される。なお、化学式中、$AcAc=C_5H_7O_2$（アセチルアセトナート）を示す。

酸化チタン薄膜を製造する製造薬剤としては、$Ti(OC_2H_5)_4$, $Ti(iOC_3H_7)_4$, $Ti(OC_4H_9)_4$, $Ti(OC_4H_9)_2C_{12}$ などのチタンアルコキシド、チタンアルコキシドにエチレングリコールなどのグリコール類、酢酸や乳酸などの酸類、トリエタノールアミンなどのアルカノールアミン類、アセチルアセトンなどのβージケトン類との付加反応物や錯体、および$TiCl_4$ などの塩化物をエタノールなどの汎用アルコール、酢酸エステルやβージトンなどの溶剤に溶解したものなどがあるが、チタンアルコキシドをアセチルアセトンに溶解反応したβージケトン錯体溶液が高活性、高透過率の点で特に好ましい。

また、光触媒機能を促進させるために公知の種々の方法を適宜採用することも可能であり、例えば透明性を失わない程度に、微量の金属（金、白金、パラヂウム、銀、銅等）を酸化チタン膜に担持させることもできる。

さらに、電磁波シールド機能を付与するためにプレコート層の上にＩＴＯ膜を形成させて導電性を付与し更にその上に酸化チタン膜を形成することも可能である。

以上詳述したように、本発明にかかる酸化チタン光触媒構造体及びその製

造方法は、透光性基体上に少なくとも光触媒活性を有すると同時に波長５５０ｎｍの光に対する光直線透過率が５０％以上有する酸化チタン薄膜を形成することを特徴とするもので、これにより、優れた光触媒作用と光透過性を有し、しかも、特に透明性が要請される種々の構造物を構成する部材に光触媒作用を兼ね備えさせることを可能にした酸化チタン光触媒構造体及びその製造方法を得ているものである。

産業上の利用可能性

以上のように、本発明にかかる酸化チタン光触媒構造体は、特に透明性が要請される種々の構造物、例えば、ガラス窓等を構成する部材としてこの酸化チタン光触媒構造体を用いることができることになり、例えば、室内の炭酸ガスや大気汚染物質（ＮＯx やＳＯx など）の除去、脱臭・抗菌・防汚・防かび等の作用を特別な装置を用いることなく窓ガラス自体によって行なわせるという画期的な効果を得ることが可能になる。しかも、窓ガラスに適用して室内の清浄化を行う場合には、太陽光を極めて有効に利用できるという大きなメリットが得られる。さらに、特に、近年多くみられるガラス材を多用したビル建築物等に適用すれば、その居住空間の清浄化に対する効果ははかりしれないものとなる。また、その他にも、例えば、かびや腐蝕を極力嫌うカメラ等の精密機器その他を保管するためのガラス戸等を備えた保管棚のガラス戸等にも用いることができる。さらに、他にも透明な硝子の所望される種々の用途に使用でき、例えば、種々の電子機器あるいは計器用のガラスカバー、蛍光灯管、電球などの照明器具、レンズ、コップなどにも適用でき、その応用範囲は極めて広い。

* C L M S *

請 求 の 範 囲

1．透光性基体上に、少なくとも、光触媒活性を有すると同時に波長５５０ｎｍの光に対する光直線透過率が５０％以上有する酸化チタン薄膜を形成してなる酸化チタン光触媒構造体。

2．前記酸化チタン薄膜の膜厚が０．１μｍ～５μｍであることを特徴とする請求の範囲１に記載の酸化チタン光触媒構造体。

3．前記酸化チタン薄膜は少なくともアナターゼ結晶を含むものであることを特徴とする請求の範囲１又は２に記載の酸化チタン光触媒構造体。

4．前記透光性基体と酸化チタン薄膜との間に光透過性を有するプレコート薄膜を設けたことを特徴とする請求の範囲１ないし３のいずれかに記載の酸化チタン光触媒構造体。

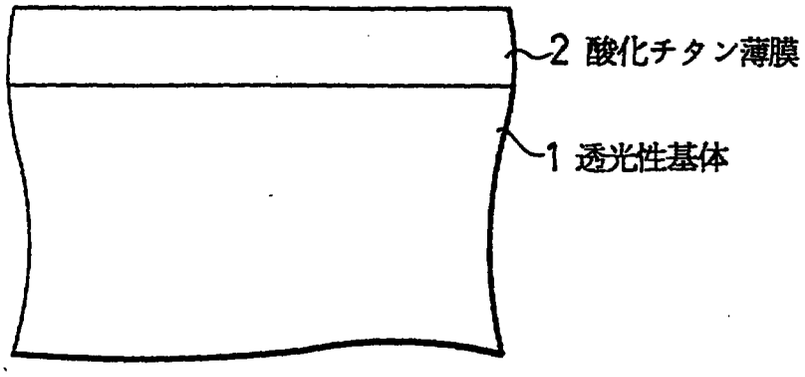
5．前記プレコート薄膜の膜厚が０．０２～０．２μｍであることを特徴とする請求の範囲４に記載の酸化チタン光触媒構造体。

6．前記透光性基体がガラスであることを特徴とする請求の範囲１ないし５のいずれかに記載の酸化チタン光触媒構造体。

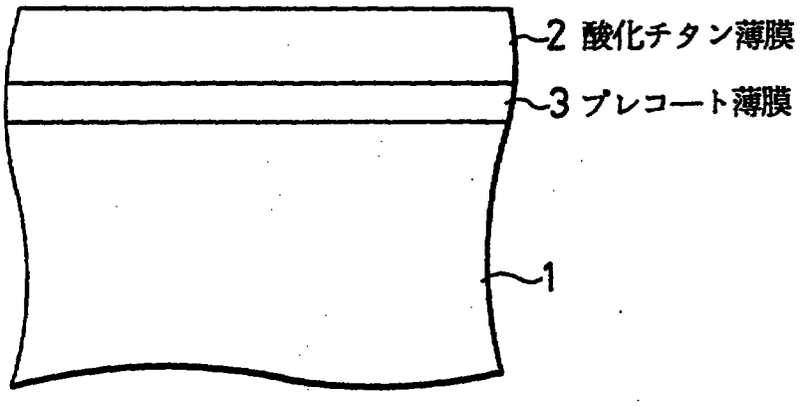
7．前記プレコート薄膜がSiO_2を主成分とする材料からなることを特徴とする請求の範囲４ないし６のいずれかに記載の酸化チタン光触媒構造体。

8．透光性基体の上に酸化チタン薄膜をパイロゾル法、ディップ法、印刷法又はＣＶＤ法によって成膜する工程を含む製造工程によって請求の範囲１ないし７に記載の酸化チタン光触媒構造体を製造することを特徴とする酸化チタン光触媒構造体の製造方法。

第 1 図



第 2 図

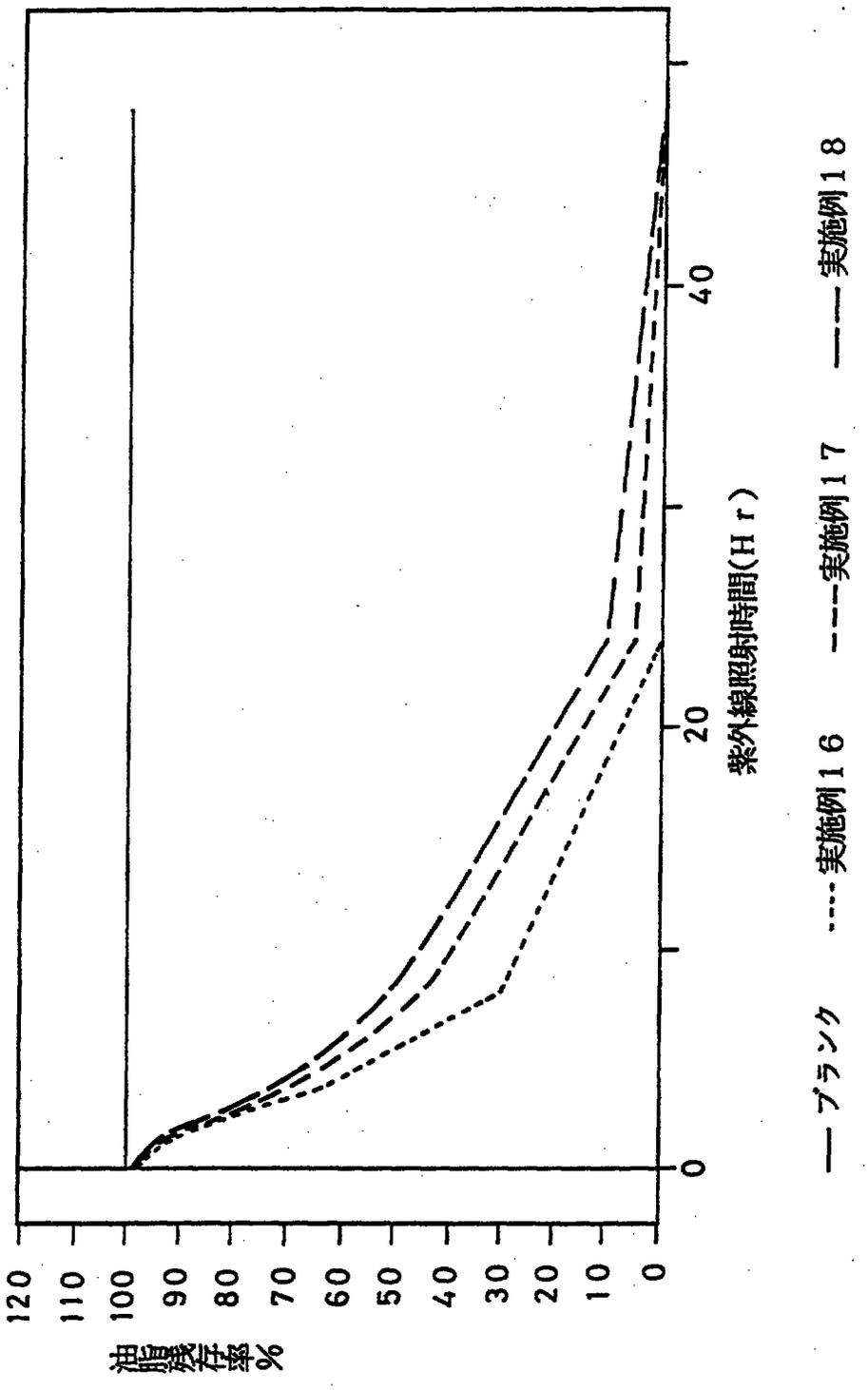


第 3 図

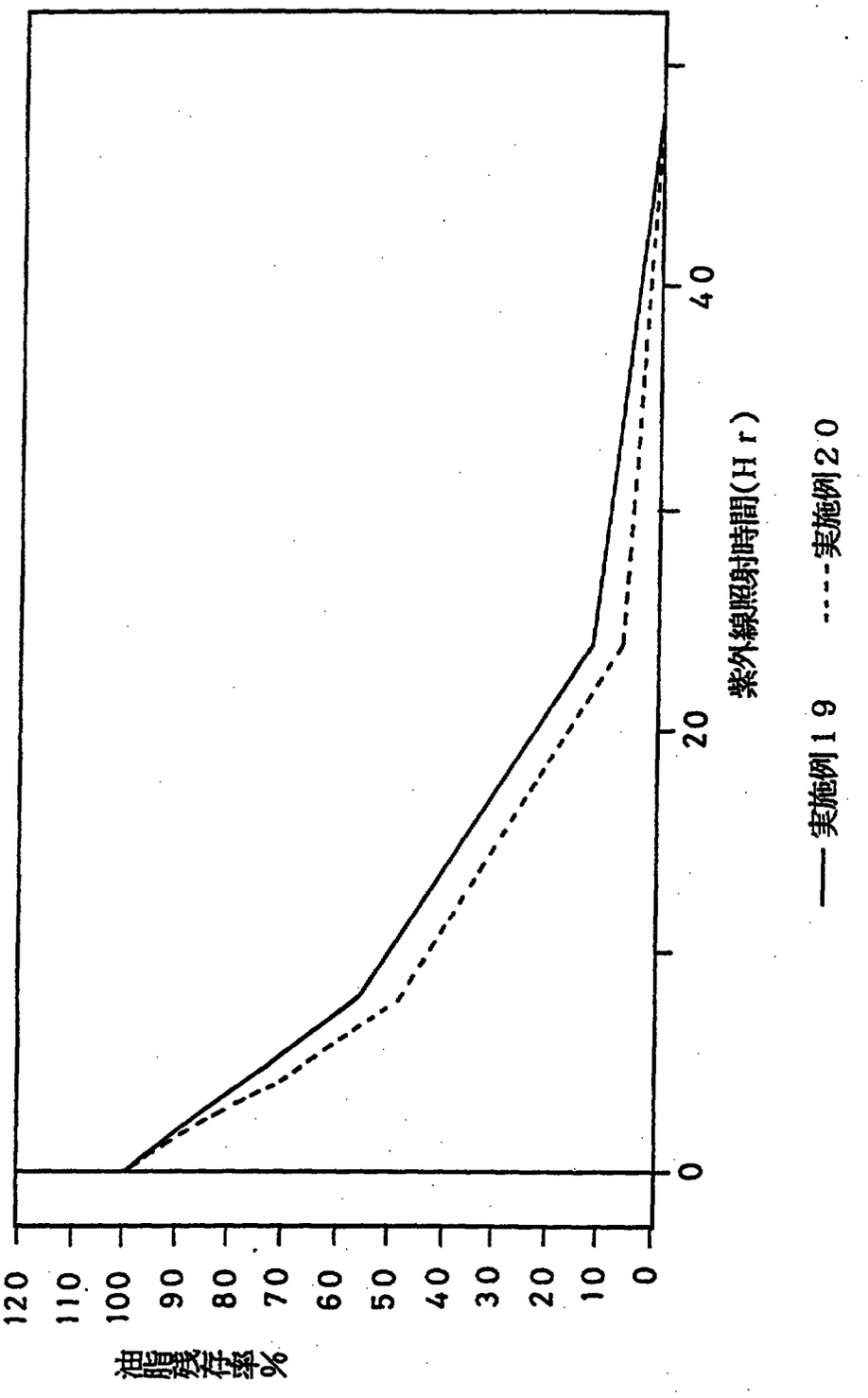
	透明基板	プレコート膜 組成 厚さ	酸化チタン薄膜	透過率	分解活性
実施例		(μm)	(μm)	(%)	(μl/min)
1	SLG	無し - - -	4.8	70	10.5
2	SLG	無し - - -	0.3	75	0.15
3	SLG	無し - - -	1.5	69	2.43
4	SLG	無し - - -	2.3	80	8.10
5	SLG	無し - - -	3.2	75	9.48
6	SLG	無し - - -	4.1	70	10.8
7	SLG	SiO2 0.1	0.1	85	1.53
8	SLG	SiO2 0.1	0.6	91	5.87
9	SLG	SiO2 0.1	1.7	86	13.1
10	SLG	SiO2 0.1	2.3	77	14.5
11	SLG	SiO2 0.1	3.0	74	15.3
12	SLG	SiO2 0.1	4.2	72	15.6
13	石英	無し - - -	0.5	86	13.2
14	石英	無し - - -	2.3	60	14.4
15	SLG	無し - - -	4.3	78	10.9
比較例					
1	SLG	無し - - -	0.05	90	0.01以下
2	SLG	無し - - -	4.3	70	0.01以下
3	SLG	無し - - -	0.1g/50cm²	10以下	24.5

SLG:ソーダライム硝子

第 4 図


油性分解活性
油脂残存率%
120
110
100
90
80
70
60
50
40
30
20
10
0
0
20
40
紫外線照射時間(Hr)
—ブランク
----実施例16
---実施例17
——実施例18

第 5 図


油脂分解活性
油脂残存率%
120
110
100
90
80
70
60
50
40
30
20
10
0
0
20
40
紫外線照射時間(Hr)
実施例19
実施例20

SPECIFICATION

TITANIUM DIOXIDE PHOTOCATALYST STRUCTURE AND METHOD FOR PRODUCING THE SAME

Technical Field

The present invention relates to a titanium dioxide photocatalyst structure that has excellent photocatalytic actions and light transmissivity and enables members of various substances, which require transparency particularly, to have photocatalytic actions. The present invention further relates to a method for producing such a titanium dioxide photocatalyst structure.

Background Art

Heretofore, there have been known photocatalysts that exhibit activities, by which the decomposition and oxidation of substances are accelerated, when irradiated with light. Recently, attempts or the like have been made to remove air pollutants such as sulfur oxides and nitrogen oxides by utilizing the photocatalysts. Moreover, attempts have been further made to use titanium dioxides as the photocatalysts (see, for example, Japanese Patent Laid-Open Nos. 6-385/1994, 6-49677/1994 and 6-39285/1994 Official Gazettes).

By the way, in recent years, there has been a growing interest in globally environmental pollution. Meanwhile, the demand for removing substances such as CO_2, NO_x and SO_x has grown. Moreover, a plan for creating amenity space by eliminating toxic substances has been devised. Thus, the demands for deodorizing living space and for making the living space antibacterial, soil- resistant and mildew-proof have grown increasingly.

It is accordingly conceived that the aforementioned titanium-dioxide photocatalyst is utilized for removing such pollutants. However, in the case of the conventional titanium dioxide photocatalysts, generally, gaseous or liquid materials to be treated are introduced into a container accommodating the photocatalyst and are thus made to be in contact with the photocatalyst, and simultaneously, light is introduced from the exterior thereto and is applied onto the photocatalyst.

Further, in such a case, for the purpose of increasing the contact area between the material to be treated and the photocatalyst and efficiently applying the light onto the photocatalyst, attempts or the like have been made to produce the photocatalyst in minute- particle form or to hold the photocatalyst on a transparent base material.

However, in the case of the aforementioned conventional titanium dioxide photocatalyst, although the

contact area between the photocatalyst and the material to be treated can be increased by, for instance, producing the photocatalyst in minute-particle form, the effective area of the photocatalyst, by which light is received, cannot be increased very much. Consequently, it is difficult to largely enhance the total catalysis effects thereof.

Further, in the case where the titanium dioxide photocatalyst is formed in film form on, for example, a glass substrate or the like, the titanium dioxide photocatalyst itself has low transparency. This is because it has been heretofore considered that methods suitable for forming a photocatalyst in film form to thereby obtain practical photocatalysis are limited to a method of forming a titanium dioxide sol on the substrate by sintering and a method of producing titanium dioxide in fine powder form, dissolving the powder by using a binder and then applying the dissolved powder onto the substrate. However, in the case of employing the former method, a photocatalyst, which has high activity and a certain measure of transparency, can be obtained, though it is necessary for obtaining the film, whose strength is sufficient for practical use, to set a sintering temperature at a value which is not lower than the softening temperature of glass. Thus, at least, it is impossible to form the photocatalyst on the glass substrate. Besides, regarding the light transmissivity, this

photocatalyst tends to become clouded. It is difficult for this photocatalyst to transmit visible light to such an extent that the transparency can be obtained. In this sense, this photocatalyst is close to opaque. In contrast, in the case of the latter method, although the step of sintering is unnecessary, the photocatalyst becomes clouded and opaque because fine titanium dioxide powder is applied to the substrate.

Further, in the case of titanium dioxide produced in film form by performing a sol-gel method and CVD method which have been well known in the field of such a kind heretofore, the transparency can be ensured, whereas the activity of the catalyst, which has a practical level, is not obtained.

Thus, all of the conventional titanium dioxide photocatalysts, which exhibit the photocatalytic activities of practical levels, are substantially opaque.

Therefore, even in the case that this conventional photocatalyst is formed on, for example, the front surface of a transparent glass substrate or the like, light applied from the back surface of the glass substrate cannot effectively reach the front surface portion of the photocatalyst. Consequently, only light applied from the front surface portion, on which the photocatalyst is not formed, of the substrate can be utilized. Hence, in the case that the

cleaning of indoor air is performed by forming this photocatalyst on, for instance, the surface of window pane, it naturally follows that the photocatalyst is formed on the surface of the glass, which faces the inside of a room. Thus, only light applied from the inside of the room that can be utilized for obtaining the photocatalytic activity. Consequently, there has been a serious defect that sunlight cannot be utilized therefor.

Thus, in the case of the conventional titanium dioxide photocatalyst, titanium dioxide, which performs the photocatalysis, itself is substantially opaque. Consequently, there occurs a limit to the enhancement of the photocatalytic activity. Moreover, the range of application of the photocatalyst is extremely limited.

The present invention is accomplished against the aforementioned background. The present invention aims at providing a titanium dioxide photocatalyst structure that has excellent photocatalytic actions and light transmissivity and enables members of various substances, which require transparency particularly, to have photocatalytic actions and further aims at providing a method for producing such a photocatalyst structure.

Disclosure of Invention

To solve the aforesaid problem, in accordance with

the present invention, there is provided a titanium dioxide photocatalyst structure (Structure 1) comprising:

a titanium dioxide film having at least photocatalytic activity and light transmittance, which is not less than 50 % for light having a wavelength of 550 nm, is formed on a transparent substrate.

As an embodiment of Structure 1, there is provided a photocatalyst structure (Structure 2), wherein the titanium dioxide film is 0.1 to 5 μ m in thickness.

As an embodiment of Structure 1 or Structure 2, there is provided a photocatalyst structure (Structure 3), wherein the titanium dioxide film contains at least anatasecrystals.

As an embodiment of Structure 1, Structure 2 or Structure 3, there is provided a photocatalyst structure (Structure 4), wherein a precoat film having transparency is disposed between the transparent substrate and the titanium dioxide film.

As an embodiment of Structure 4, there is provided a photocatalyst structure (Structure 5), wherein the precoat film is 0.02 to 0.2 μ m in thickness.

As an embodiment of Structure 1, Structure 2, Structure 3, Structure 4 or Structure 5, there is provided a photocatalyst structure (Structure 6), wherein the transparent substrate is made of glass.

As an embodiment of Structure 1, Structure 2, Structure 3, Structure 4, Structure 5 or Structure 6, there is provided a photocatalyst structure (Structure 7), wherein the precoat film is made mainly of SiO_2.

Further, in accordance with the present invention, there is provided a method (Structure 8) for producing a titanium dioxide photocatalyst structure which is one of Structure 1 to Structure 7. In the case of this method, the titanium dioxide photocatalyst structure is produced by performing a producing process which includes the step of forming a titanium dioxide film on a transparent substrate by performing what is called a pyro-sol method, a dipping method, a printing method or a CVD method.

In accordance with the foregoing Structure 1, a titanium dioxide film, which has at least photocatalytic activity and light transmittance corresponding to light having a wavelength of 550 nm is not less than 50 %, is formed on a transparent substrate. Thereby, the titanium dioxide photocatalyst structure can have excellent photocatalytic action and optical transmissivity. Moreover, the titanium dioxide photocatalyst structures can be used as members composing various structures such as a glass window, which are especially required to have light transmissivity.

This is owing to the fact that as a result of setting the

titanium dioxide film in such a manner that the light transmittance corresponding to light having the wavelength of 550 nm is not less than 50 %, the substantially increasing of light irradiation efficiency required to obtain photocatalytic activities can be easily achieved and simultaneously, the transparency corresponding to visible light can be ensured. Namely, if setting the titanium dioxide film in such a manner that the light transmittance corresponding to light having the wavelength of 550 nm is not less than 50 %, the titanium dioxide film inevitably has the transmissivity corresponding to light, which gives the photocatalytic activity (and which has the wavelength of about 400 nm), in such a way that the degree of the transmissivity is sufficient to effectively utilize light applied thereto from the front and back thereof. Therefore, when both of the front and back surfaces of this titanium dioxide photocatalyst structure are irradiated with different light, respectively, the light rays respectively coming from both of the surfaces thereof reach the surface portion, which is in contact with the exterior, of the titanium dioxide film in such a manner as to be added to each other. Namely, the efficiency in applying light onto the surface porion of the titanium dioxide film can be substantially increased. Thereby, the photocatalytic activity of the surface portion of

the titanium dioxide film can be substantially increased in response to this, so that excellent photocatalytic activity can be obtained. Simultaneously, as a consequence of setting the titanium dioxide film in such a manner that the light transmittance corresponding to light having the wavelength of 550 nm is not less than 50 %, the sufficient transparency corresponding to visible light can be secured inevitably. Consequently, this titanium dioxide photocatalyst structure can be used as a member of various structures especially required to have the transparency, for example, a glass window. The present invention can have distinguished advantages in that actions of eliminating carbon dioxide and air pollutants (for example, NOx and SOx) from indoor space, of deodorizing the indoor space and of making the indoor space antibacterial, soil-resistant and mildew-proof are achieved by the window pane itself without using special equipment. Additionally, the present invention can obtain eminent merits in that in the case of cleaning the room by applying the photocatalyst structure to the window pane, sunlight can be extremely utilized.

Moreover, especially, in the case of applying the photocatalyst structure of the present invention to a building or the like, in which glass materials are highly used, of the type that has become common in recent years, the photocatalyst structure of the present invention has

immeasurable advantages in cleaning the living space. In addition, the photocatalyst structure of the present invention can be applied to a glass door or the like of a shelf, which includes the door or the like, for storing, for instance, precision devices such as a camera which should be kept away from molds and corrosion. Thus, the range of application of the photocatalyst structure of the present invention is extremely wide.

In accordance with the foregoing Structure 2, a titanium dioxide film having sufficient photocatalytic activity and simultaneously having the light transmittance, which is not less than 50 % correspondingly to light having a wavelength of 550 nm, can be obtained by setting the thickness of the titanium dioxide tin film at a value of 1 to 5 μ m. In the case that the thickness of the photocatalyst structure is less than 0.1 μ m, sufficient photocatalytic activity cannot be obtained. In contrast, in the case that the thickness of the photocatalyst structure exceeds 5 μ m, the light transmittance corresponding to the light having the wavelength of 550 nm is less than 50 %. Consequently, sufficient transparency cannot be obtained.

In accordance with Structure 3, the titanium dioxide film contains anatase crystals. Thereby, the photocatalyst structure can further excels in photocatalytic activity.

In accordance with Structure 4, a precoat film having

transparency is disposed between the transparent substrate and the titanium dioxide film. Thus, the material of the transparent substrate penetrates into the titanium dioxide film, so that the photocatalytic activity of the titanium film can be prevented from being degraded. Moreover, the range of materials of the transparent substrate to choose can be extended. Furthermore, in the case of forming a titanium dioxide film directly on the transparent substrate, the titanium dioxide film should have a thickness sufficient to the extent that even when the material of the transparent substrate penetrates into the titanium dioxide film, the material cannot reach titanium dioxide on which charge separation action should be exerted. The present invention, however, eliminates the necessity of making the film thick to such an extent. Thus, even when the titanium dioxide film is made to be extremely thin regardless of what kind of materials the substrate employs, the photocatalytic activity can be sufficiently enhanced.

In the case that the thickness of the precoat film is 0.02 to 0.2 μ m similarly as in the case of Structure 5, even when taking materials, which can be employed as those of the precoat film, into consideration, the photocatalyst structure of the present invention can obtain advantages in that sufficient transparency can be ensured and that the penetration of the material of the substrate can be blocked.

Conversely, in the case that the thickness of the precoat film is less than 0.02 μ m, it is difficult to have a sufficient effect on the blockage of the penetration of the material. Further, even in the case that the film, whose thickness exceeds 2 μ m, is formed, the photocatalyst structure cannot have further advantageous effects on the blockage of the penetration of the material. Moreover, an operation of forming the film becomes complicated. Furthermore, if the film is made of some material, the sufficient transparency cannot be ensured.

In the case that glass is used as the transparent substrate similarly as in the case of Structure 6, the extremely wide range of application of the photocatalyst structure of the present invention can be achieved, as previously described. In this case, if the precoat film is made of SiO_2 similarly as in the case of Structure 7, the best transparency and the highest effects on the blockage of can be secured.

Furthermore, in accordance with Structure 8, the titanium dioxide photocatalyst structure according to one of Structure 1 to Structure 7 can be relatively easily obtained.

Brief Description of Drawings

FIG. 1 is a partially sectional diagram for illustrating

the configuration of a titanium dioxide photocatalyst structure according to Example 1;

FIG. 2 is a partially sectional diagram for illustrating the configuration of a titanium dioxide photocatalyst structure according to Example 7;

FIG. 3 is a diagram for showing a table in which the thickness of films of Examples according to the present invention and Comparative Examples, results of measurement of photocatalytic activities thereof and results of measurement of the light transmittance thereof are presented;

FIG. 4 is a diagram for showing a graph which represents results of measurement of fat splitting activities of Example 16 to Example 18 according to the present invention; and

FIG. 5 is a diagram for showing a graph which represents results of measurement of fat splitting activities of Example 19 and Example 20 according to the present invention.

Best Mode for Carrying Out the Invention

(Example 1)

FIG. 1 is a partially sectional diagram for illustrating the configuration of a titanium dioxide photocatalyst structure according to Example 1 of the photocatalyst

structure of the present invention. Hereinafter, Example 1 of the titanium dioxide photocatalyst structure and a method for producing this titanium dioxide photocatalyst structure will be described with reference to FIG. 1.

As shown in FIG. 1, in the case of this example of the titanium dioxide photocatalyst structure, a titanium dioxide film 2 is formed on a transparent substrate 1.

The transparent substrate 1 is a soda lime glass substrate whose thickness, longitudinal size and lateral size are 1, 100 and 50 mm, respectively.

The film 2 is a titanium dioxide film which contains anatase crystals and is 4.8 μ m in thickness.

The aforementioned titanium dioxide photocatalyst structure was produced by performing the following process.

First, a transparent substrate 1 was produced by extracting a soda lime glass whose thickness, longitudinal size and lateral size were 1 mm, 100 mm and 50 mm, respectively.

Next, a raw-material solution, in which the concentration of titanium isopropoxide was adjusted to 0.5 mol/L, was made by dissolving titanium isopropoxide in acetylacetone solvent as the material of a titanium dioxide film.

Subsequently, the transparent substrate 1 was set in

a pyro-sol film forming device. Further, the transparent substrate 1 was preliminarily heated to 500 degrees centigrade. Moreover, the raw-material solution underwent ultrasonic atomization and was then introduced to the surface of the transparent substrate 1 at a rate of 20 ml/min. Then, an operation of forming a film was performed in the period of about 60 minutes. Consequently, there had been obtained a titanium dioxide photocatalyst structure in which this titanium dioxide 2, whose thickness was 4.8 μ m, was formed on the transparent substrate 1. Incidentally, according to a result of analysis of this titanium dioxide film 2 based on X-ray diffraction, it was verified that this film 2 contained anatase crystals.

Next, the photocatalytic activity and light transmittance of the obtained titanium dioxide photocatalyst structure were measured by performing the following method.

Method for Measuring Photocatalytic Activity

The titanium dioxide photocatalyst structure was placed in the bottom of a cylindrical glass gastight enclosure, whose capacity was 1.5 L, in such a way that the titanium dioxide film 2 was the upper part thereof. Then, acetaldehyde was introduced into this enclosure so that the concentration of acetaldehyde was 1300 ppm. Next, the

titanium dioxide photocatalyst structure was irradiated with light from above the surface of the titanium dioxide film 2 by using three 10-W black lights. At that time, the illuminance measured on the surface of the titanium dioxide film 2 was 1.2 mW/cm2. Thereafter, the quantitative analysis of acetaldehyde contained in the glass gastight enclosure was performed by using a gas chromatograph with FID. Thus, the decrement of the amount of acetaldehyde, which was caused after the photocatalyst structure was irradiated with light, was obtained. Further, the obtained decrement of the amount of acetaldehyde was defined as the degree of the photocatalytic activity.

Method for Measuring Light Transmittance

Titanium dioxide photocatalyst structure of Example 1 was first set in a device for measuring light transmittance (namely, UV-3100PC manufactured by Shimadzu Corporation). Then, the light transmittance corresponding to light, whose wavelength is 550 nm, was measured.

According to a result of the measurement by the herein-aforementioned method, what is called the decomposition activity was 10.5 μ l/min and the light transmittance was 70 %. Thus, it was verified that this titanium dioxide photocatalyst structure had excellent photocatalytic activity and sufficient transparency.

Then, the titanium dioxide photocatalyst structure was again placed in the bottom of the aforesaid cylindrical glass gastight enclosure by being turned upside down, namely, in such a way that the titanium dioxide film 2 faced the bottom of the enclosure. Subsequently, the photocatalytic activity of the photocatalyst structure was measured by irradiating the photocatalyst with light coming from the similar direction, namely, from the side, on which the titanium dioxide film 2 was not formed, of the transparent substrate 1. At that time, it was verified that the photocatalytic activity, whose value was nearly close to that obtained in the aforementioned case, could be obtained. This result shows that light applied from the back surface of the transparent substrate 1 contributes to the photocatalytic activity of the titanium dioxide film 2 as well as the light applied from the front surface of the transparent substrate 1 and that the photocatalytic effects thereof can be considerably enhanced by applying light to both of the sides of the photocatalyst structure.

(Example 2 to Example 6)

These Examples have structures, which are similar to the structure of Example 1 except that the thickness of the titanium dioxide film 2 is different from that of the film 2 of Example 1, and are produced by a producing method similar to that employed in the case of Example 1. Data

representing the thickness of each Example and results of measurement of the photocatalytic activity and light transmittance are shown in FIG. 3 in tabular form. Further, the detailed description of the data is omitted.

As is seen from the table of FIG. 3, each of these Examples has excellent photocatalytic activity and sufficient transparency.

(Example 7 to Example 12)

These Examples have structures, which are similar to the structure of Example 1 except that a precoat film 3 constituted by a SiO2 film is formed between the titanium dioxide film 2 and the transparent substrate 1 by a dip coating as illustrated in FIG. 2, and are produced by a producing method similar to that employed in the case of Example 1. Data representing the thickness of each Example and results of measurement of the photocatalytic activity and light transmittance are shown in FIG. 3 in tabular form. Further, the detailed description of the data is omitted.

As is seen from the table of FIG. 3, even when the thickness of the titanium dioxide film 2 is reduced, excellent photocatalytic activities are exhibited, in comparison with Example 1 to Example 6 which do not have the precoat film 3. Thus, further higher transparency can be ensured.

(Example 13 to Example 14)

These Examples have structures, which are similar to the structure of Example 1 except that the soda lime glass of Example 1 is replaced with quartz glass, and are produced by a producing method similar to that employed in the case of Example 1. Data representing the thickness of each Example and results of measurement of the photocatalytic activity and light transmittance areshown in FIG. 3 in tabular form. Further, the detailed description of the data is omitted.

As is seen from the table of FIG. 3, even though the Examples do not have the precoat film 3, excellent photocatalytic activities are exhibited, because quartz glass is used as the material of the transparent substrate 1. In addition, these Examples have sufficient transparency.

(Example 15)

This Example has a structure, which is similar to the structure of Example 1 except that the temperature at the time of forming the titanium dioxide film is changed into 380 degrees centigrade and that the step of performing heat treatment in the period of 60 minutes at the temperature of 400 degrees centigrade under airatmosphere is added, and are produced by a producing method similar to that employed in the case of Example 1. Data representing the thickness of each Example and results of measurement of the

photocatalytic activity and light transmittance are shown in FIG. 3 in tabular form. Further, the detailed description of the data is omitted.

As is seen from the table of FIG. 3, each of these Examples has excellent photocatalytic activity and sufficient transparency.

(Example 16)

In the case of this Example, the precoat film 3 constituted by a SiO_2 film having a thickness of 0.06 μ m was formed on the transparent substrate 1. Moreover, the titanium dioxide film 2 having a thickness of 0.8 μ m was formed by what is called a dipping method.

A soda lime glass plate, whose thickness, longitudinal size and lateral size are 1 mm, 100 mm and 50 mm, respectively, was used as the transparent substrate 1. This transparent substrate 1 was slowly dipped into a vessel, which contains silicon alkoxide solution (incidentally, the trade name thereof was "ATOLON NSi-500" and was manufactured by Nippon Soda Co., Ltd.) of 800 ml and has a width of 100 mm, a depth of 50 mm and a height of 200 mm, respectively. Thereafter, this transparent substrate 1 was pulled up therefrom at a speed of 10 cm/min. This substrate was then dried at the temperature of 150 degrees centigrade. Subsequently, the substrate was sintered at the temperature of 500 degrees centigrade in the period of 1 hour. Thus, a

SiO2 film, whose thickness was 0.06 μ m, was formed on the transparent substrate 1 as the precoat film 3.

Next, the glass substrate provided with the precoat film was slowly dipped into 800 ml of an organic titanium solution for dipping (incidentally, the trade name thereof was "ATOLON NTi-500" and was manufactured by Nippon Soda Co., Ltd.), which was obtained by causing titanium tetraisoproxide to react with organic solvent. Thereafter, the substrate was slowly pulled up therefromat a speed of 10 cm/min. This substrate was then driedat the temperature of 120 degrees centigrade. Subsequently, the substrate was sintered at thetemperature of 500 degrees centigrade in the period of 1hour. Thus, a titanium dioxide film was formed on the precoat film. This process for forming a titanium dioxide film, which had the steps of dipping the substrate into chemicals and then drying and sintering the substrate, was repeated 10 times. Thus, the thickness of the titanium dioxide became 0.8 μ m, so that the titanium dioxide photocatalyst structure of this Example was obtained.

The titanium dioxide photocatalyst structure obtained in this way has the light transmittance of 81 % correspondingly to light having the wavelength of 550 nm. Further, regarding this Example, a fat splitting activity was taken up as one of the photocatalytic activities and

was evaluated as follows.

Evaluation of Fat Splitting Activity

The aforementioned titanium dioxide photocatalyst structure was extracted as a 50-by-50-mm test piece. Then, the entire surface of the test piece was softly wiped with tissue paper which had soaked commercially available salad oil. Thus, an amount of applied salad oil was adjusted to 0.1 mg/cm2 by applying the salad oil thereto and wiping the salad oil therefrom. The initial amount of salad oil was measured by weighing the glass plate by using a precision balance whose weight accuracy is 0.1 mg. This substrate, to which the salad oil had been applied, was then irradiated with ultraviolet rays coming from ultraviolet lamps (namely, three 10-W black lights FL10BLB manufactured by Matsushita Electric Works,Ltd., were arranged in a low and were used for applying the ultraviolet rays) for a predetermined time period, by regulating the distance between each ultraviolet lamp and the surface of the test piece in such a manner that the ultraviolet intensity measured by the ultraviolet-intensity detector (manufactured by Ultraviolet Corporation) was 3 mW/cm2. After the predetermined time period has passed, the amount of the split salad oil (fat) was found by measuring the weight of the glass substrate.

FIG. 4 illustrates a graph which shows the fat splitting

characteristics of the photocatalyst structure of Example 16. Incidentally, in the graph of FIG. 4, the vertical axis represents the rate of residual fat (in %); and the horizontal axis a time period (in hours) in which ultraviolet was applied. Further, similarly as in the herein-aforementioned case, salad oil was applied to the glass substrate provided only with a precoat film, on which no titanium dioxide film was formed. Then, ultraviolet was applied thereto (from the black light). After the predetermined time period passed, a change in weight of the glass substrate was measured. Thus, the resultant data was obtained as data in the case of a "blank" test piece. The result in this case is also shown in the graph of FIG. 4. As is obvious from FIG. 4, this titanium dioxide photocatalyst structure has excellent fat splitting activity.

(Example 17)

In the case of this Example, the precoat film 3 constituted by a SiO2 film having a thickness of 0.06 μ m was formed on the transparent substrate 1.

Further, a titanium dioxide film having a thickness of 0.6 μ m was formed thereon by performing what was called a spraying method.

Similarly as in the case of Example 16, the SiO2 film having a thickness of 0.06 μ m was formed as the precoat film 3 by using a soda lime plate whose thickness,

longitudinal size and lateral size are 1 mm, 100 mm and 50 mm, respectively.

Next, the transparent substrate 1, on which this precoat film 3 was formed, was leaned against the inner part of a box-type heater which had been heated to 500 degrees centigrade. Then, 10 shots of an organic solvent solution of titanium acetylacetonato obtained by causing a reaction between 140 g of titanium tetraisopropoxide and 200 g of acetylacetone were sprayed onto the precoat film 3 of the transparent substrate1. Subsequently, the titanium dioxide film 2 having a thickness of 0.6 μ m was formed by performing thermal decomposition thereon.

The light transmittance of the titanium dioxide photocatalyst structure corresponding to light having the wavelength of 550 nm was 78 %. Further, the fat splitting activity acting as the photocatalytic activity was measured similarly as in the case of Example 16. A result of this measurement is shown in FIG. 4 together with a result of the measurement in the case of Example 16.

(Example 18)

In the case of this Example, the precoat film 3 constituted by a SiO2 film having a thickness of 0.06 μ m was formed on the transparent substrate 1.

Further, a titanium dioxide film having a thickness of 0.4 μ m was formed thereon by performing what was called a

printing method.

Similarly as in the case of Example 16, the SiO_2 film having a thickness of 0.06 μ m was formed as the precoat film 3 by using a soda lime plate whose thickness, longitudinal size and lateral size are 1 mm, 100 mm and 50 mm, respectively.

Next, a screen process printing was performed by a printing machine, which was provided with a 400-mesh screen, on the aforementioned precoat film 3 by using a solvent obtained by causing a reaction and dissolution among 70 g of titanium tetraisopropoxide, 100 g of ethyl cellulose and 1200 g of organic solvent. Upon completion of printing, the film was put into a stationary state in the period of 5 min. Then, the leveling of the film was performed. Thereafter, the film was sintered in an electric furnace which had been heated to 500 degrees centigrade. This printing and sintering process was repeated 5 times. Thus, the thickness of the titanium dioxide became 0.4 μ m, so that the titanium dioxide photocatalyst structure of this Example was obtained.

The light transmittance of this photocatalyst structure corresponding to the wavelength of 550 nm was 86 %. Further, similarly as in the case of Example 16, the fat splitting activity was measured. Thus, a result of this measurement was obtained as shown in the graph of

FIG. 4.

(Example 19)

In the case of this Example, the precoat film 3 constituted by a SiO_2 film having a thickness of 0.04 μ m was formed on the transparent substrate 1 by performing the pyro-sol method. Moreover, the titanium dioxide film 2 having a thickness of 0.4 μ m was formed thereon by the dipping method.

The transparent substrate 1 constituted by a soda lime glass plate, whose thickness, longitudinal size and lateral size are 1 mm, 100 mm and 50 mm, respectively, was set in the pyro-sol film forming device. Subsequently, organic silicon solution (incidentally, the trade name thereof was "ATOLON NSi-500" and was manufactured by Nippon Soda Co., Ltd.) underwent ultrasonic atomization and was then introduced to the glass substrate, which had been heated to 500 degrees centigrade, at a rate of 20 ml/min in the time period of 2 min. Thus, the silicon-dioxide precoat film 3, whose thickness was 0.04 μ m, was formed.

Next, similarly as in the case of Example 16, a titanium dioxide film was formed on this precoat film 3 by performing the dipping method. This process for forming a titanium dioxide film, which had the steps of dipping the substrate into chemicals and then soaking,

drying and sintering the substrate, was repeated 5 times. Thereby, the thickness of the titanium dioxide became 0.4 μm, so that the titanium dioxide photocatalyst structure, in which the transparent titanium dioxide film 2 was formed, was obtained.

The light transmittance of this photocatalyst structure corresponding to the wavelength of 550 nm was 89 %. Further, similarly as in the case of Example 16, the fat splitting activity was measured. Thus, a result of this measurement was obtained as shown in the graph of FIG. 5.

(Example 20)

In the case of this Example, the precoat film 3 constituted by a SiO_2 film having a thickness of 0.06 μm was formed on the transparent substrate 1. Moreover, the titanium dioxide film 2 having a thickness of 0.6 μm was formed thereon by what is called a CVD method.

The transparent substrate 1 constituted by a soda lime glass plate, whose thickness, longitudinal size and lateral size are 1 mm, 100 mm and 50 mm, respectively, was used as the transparent substrate 1. Moreover, the precoat film 3, which was made of silicon dioxide and was 0.06 μm in thickness, was formed by performing the same method as used in the case of Example 16.

Next, the transparent substrate 1, on which this

precoat film 3 was formed, was set in an atmospheric pressure CVD film forming device. Further, titanium tetraisopropoxide was prepared in a carbureter heated to 200 degrees centigrade. Then, gaseous nitrogen was introduced into the carbureter at the flow rate of 50ml/min to thereby cause the bubbling of titanium tetraisopropoxide. Subsequently, the vapor of titanium alkoxide was introduced through a heated conduit into a film forming portion in which the glass substrate was set. The film forming portion was heated to 500 degrees centigrade. Furthermore, air was also introduced thereinto at the rate of 200 ml/min. Thus, an operation of forming a film was performed in the period of 5 minutes. Thereby, the titanium dioxide film 2 having a thickness of 0.6 μ m was formed on the precoat film 3, so that the titanium dioxide photocatalyst structure was obtained.

The light transmittance of this photocatalyst structure corresponding to the wavelength of 550 nm was 84 %. Further, similarly as in the case of Example 16, the fat splitting activity was measured. Thus, a result of this measurement was obtained as shown in the graph of FIG. 5.

(Comparative Example 1)

This Comparative Example has a structure, which is similar to the structure of Example 1 except that the

thickness of the titanium dioxide film 2 is small, namely, 0.05 μ m, and was produced by a producing method similar to that employed in the case of Example 1. Data representing the thickness of this Comparative Example and results of measurement of the photocatalytic activity and light transmittance are shown in FIG. 3 in tabular form. Further, the detailed description of the data is omitted.

As is seen from the table of FIG. 3, this Comparative Example has good transparency but exhibits little photocatalytic activity.

(Comparative Example 2)

This Example has a structure, which is similar to the structure of Example 1 except that the temperature at the time of forming the titanium dioxide film was changed into 380 degrees centigrade, and was produced by a producing method similar to that employed in the case of Example 1. Data representing the thickness of this Comparative Example and results of measurement of the photocatalytic activity and light transmittance are shown in FIG. 3 in tabular form. Further, the detailed description of the data is omitted. Incidentally, according to a result of analysis of the titanium dioxide film 2, which was produced in this way, based on X- ray diffraction, it was verified that this film 2 did not contained anatase crystals at all.

As is seen from the table of FIG. 3, thisComparative

Example has sufficient transparency but exhibits little photocatalytic activity.

(Comparative Example 3)

This Example has a structure, which is similar to the structure of Example 1 except that the titanium dioxide film 2 was formed by using a method of applying 0.1 g of a solution, which was obtained by dispersing titanium dioxide powder (namely, "P-25" manufactured by NIPPON AEROSIL CORPORATION) into water, to the substrate, instead of the pyro-sol method, and was produced by a producing method similar to that employed in the case of Example 1. Data representing the thickness of this Comparative Example and results of measurement of the photocatalytic activity and light transmittance are shown in FIG. 3 in tabular form. Further, the detailed description of the data is omitted.

As is seen from the table of FIG. 3, this Comparative Example has high photocatalytic activity but has little transparency.

Incidentally, there is no particular restrain on the material of the transparent substrate used in the photocatalyst structure of the present invention, as long as the transparent substrate has optically predetermined transparency. To adduce actual examples, pyrex glass, quartz glass, lead glass and soda lime glass and so forth

may be employed. Practically, inexpensive soda lime glass is mainly used. Further, quartz glass, which contains no alkaline ingredients such as sodium, and borosilicate glass, which contains little alkaline ingredients such as sodium, may be preferably used in the glass substrate. In the case where the transparent substrate is made of soda lime glass, the photocatalytic action of the titanium dioxide film is hindered by alkaline ingredients such as sodium, which are diffused from the substrate. It is, therefore, preferable for preventing the diffusion to provide a precoat film on the transparent substrate. In this case, the photocatalyst structure can be advantageously used even when the transparent substrate, in which alkaline ingredients such as inexpensive soda lime glass, may be diffused.

The titanium dioxide film has a thickness of 0.1 to 5 μ m. If not more than 0.1 μ m, the film exhibits the transparency but has low photocatalytic activity. Thus, the photocatalyst structure loses the practicality. In contrast, if exceeds 5 μ m, the photocatalyst structure has advantages in that high photocatalytic activity can be maintained and that the risk of coloration due to optical interference can be reduced. The photocatalyst structure, however, tends to have defects in that the film becomes clouded and inclined and that it takes

much time to peel and form a film.

Further, it is possible to utilize a titanium dioxide, which is provided in the vicinity of the surface of the film, as a photocatalyst structure by setting the thickness of the titanium dioxide film, which should be formed, at a large value, for example, 0.3 μ m to 5.0 μ m and by setting the concentration of sodium, which is contained in the titanium dioxide film, in such a manner as to change decreasingly in the direction of thickness. In this case, the precoat film can be omitted.

The precoat film has a thickness of 0.02 to 0.2 μ m. If the thickness thereof is not more than 0.02 μ m,the ability to prevent the diffusion of alkaline ingredients is reduced. In contrast, if the thickness thereof is not less than 0.2 μ m, there is no hindrance to the ability to prevent the diffusion of alkaline ingredients. However, the light transmissivity is reduced and an operation of forming a film becomes complex. Because the diffusion of alkaline ingredients such as sodium from the substrate is prevented by the precoat film, the thickness of the titanium dioxide film can be reduced. Moreover, the titanium dioxide film, whose transparency is further higher in the visible range, can be formed.

As long as the light transmittance in the visible range is high and the diffusion of sodium from the substrate

can be prevented, there is no restrain on the composition of a precoat film. For instance, a silicone dioxide film, a tin oxide film, an indium-doped tin oxide film, an indium oxide film, a tin-doped indium oxide film, a germanium oxide film, an aluminum oxide film, zirconium oxide film and a SiO_2+MO_X film (incidentally, MO_X represents a kind of metallic oxide selected from the group of P_2O_5, B_2O_3, ZrO_2, TiO_2 and Ta_2O_5) can be cited as examples of the precoat film. From the view of the ability to prevent the diffusion of alkaline ingredients, a silicone dioxide film or a film, in which 5 % by weight of P_2O_5 is added to SiO_2, is particularly preferable

Moreover, the condition necessary to obtain a titanium dioxide film, which has a high photocatalytic activity, is that this film contains anatase crystals. When the temperature, at which the film is formed or at which the heat treatment is performed after forming the film, is high, the anatase crystals causes phase transition. As a result, a part of the anatase crystals are changed into rutile crystals. Therefore, an anatase-type titanium dioxide film containing rutile crystals is preferably used. It is, however, undesired that all of the anatase crystals are changed into rutile crystals at a high temperature. This is because of the fact that in such a case, owing to the phase transition, the titanium dioxide becomes clouded and thus the light transmittance in the

visible range is decreased.

In the case of the photocatalyst structure of the present invention, although the pyro-sol method is the most suitable for forming a film, commonly known methods for forming films can be employed for forming both of the precoat film and the titanium dioxide film. Namely, a sputtering method, an electron beam evaporation method, an ion plating method, a chemical vapor deposition (CVD) method, a spraying method, a dipping method and so forth may be applied to the photocatalyst structure of the present invention by devising a process for controlling the formation of a film. Incidentally, methods, such as the pyro-sol method and the spraying method, for spraying a mist at normal pressure are preferable, because the application of such methods to the case of actually and industrially manufacturing photocatalyst structures can be achieved by spraying a mist during a glass plate is still hot in the process of cooling the glass plate which is being produced. Additionally, film forming methods, in which a substrate should be maintained at a high temperature, which is not lower than the softening temperature of glass, for example, at a high temperature, which is not lower than 600 degrees centigrade, are undesired because such methods cause the deformation of the substrate and accelerate the diffusion of alkaline ingredients.

What is called the pyro-sol method is desired as the method for forming films, for the following reasons. First, inexpensive titanium alkoxide of high purity is used as the material. Further, the films can be formed at a high speed. Moreover, a high-activity titanium dioxide film containing anatase crystals can be obtained in such a way as to be highly uniform and have a large area. Furthermore, the formation of the films can be achieved at a temperature which is not higher than the softening temperature of glass, namely, at a temperature which is 400 to 500 degrees centigrade or so. Such a temperature is an adequate temperature at which the diffusion of sodium can be retarded. Further, the diffusion thereof can be blocked by a precoat layer. The pyro-sol method is a kind of an atmospheric pressure chemical vapor cracking method (a CVD method) and is to form the precoat film or the titanium dioxide by carrying out the process of performing the vapor-phase transport of a mist, which has undergone the ultrasonic atomization, to the substrate, which has been heated to 400 to 550 degrees centigrade, and further thermally decomposing the mist on the substrate.

Chemicals for producing precoat films are as follows. Namely, chemicals for producing SiO_2 are silicon alkoxides, such as $Si(OCH_3)_4$, $Si(OC_2H_5)_4$ and $SiCH_3(OCH_3)_3$, and condensation products thereof and silicon halide.

Further, chemicals for producing tin oxide are $Sn(OCH_3)_4$, $Sn(OC_2H_5)_4$, $Sn(OC_4H_9)_4$, $Sn(AcAc)_4$, $Sn(OCOC_4H_{15})_4$, $Sn\,C_{l4}$ and so on. Moreover, chemicals for producing indium oxide are $In(OCH_3)_3$, $In(OC_2H_5)_3$, $InCl_3$, $In(AcAc)_3$, $In(NO)_3nH_{20}$ and so forth. Furthermore, chemicals for producing germanium oxide are $Ge(OC_2H_5)_4$, $Ge(OC_4H_9)_4$, $GeCl_4$ and so forth. Further, chemicals for producing aluminum oxide are $Al(OC_2H_5)_3$, $Al(OiC_3H_7)_3$, $Al(OC_4H_9)_3$, $Al(AcAc)_3$, $Al(NO_3)_{39}H_{20}$ and so on. Moreover, chemicals for producing phosphorus pentaoxide are $P(OC_2H_5)_3$, $PO(OCH_3)_3$, $PO(OC_2H_5)_3$, H_3PO_4, P_2O_5 and so forth. Additionally, chemicals for producing boron oxide are $B(OCH_3)_3$, $B(OC_2H_5)_3$, $B(OC_4H_9)_3$, $B(AcAc)_3$, BCl_{13}, H_3BO_3 and so on. Among these, usually available chemicals are used. Incidentally, in the chemical formula, "AcAc" designates $C_5H_7O_2$ (namely, acetylacetonato).

Manufacturing chemicals for producing titanium dioxide films are as follows: titanium alkoxides such as $Ti(OC_2H_5)_4$, $Ti(OiC_3H_7)_4$, $Ti(OC_4H_9)_4$ and $Ti(OC_4H_9)_2C_{12}$; addition products and complexes obtained from titanium alkoxide and glycols such as ethylene glycol, or acids such as acetic acid and lactic acid, or alkanolamines such as triethanolamine, or β-diketons such as acetylacetone; and chemicals obtained by dissolving chlorides such as TiC_{l4} in alcohol for general application, such as ethanol, or in

solvents such as acetic ester and β-diketone. In view of high activity and transmittance, β-diketone complex solution obtained by dissolving titanium alkoxide in acetylacetone is particularly preferable.

Further, various known methods for accelerating a photocatalytic function can be employed appropriately. For example, a trace quantity of metal (for example, gold, platinum, palladium, silver, copper and so forth) may be carried by the titanium dioxide film.

Moreover, ITO film may be formed on the precoat layer so as to impart an electromagnetic-wave shielding function thereto and thus impart conductiveness thereto. Furthermore, a titanium dioxide film may be formed thereon.

As stated in detail in the foregoing description of the embodiments, characteristic aspects of the titanium dioxide photocatalyst structure of the present invention and the methods for producing the same according to the present invention reside in that a titanium dioxide film which has at least photocatalytic activity and simultaneously has light transmittance corresponding to light having a wavelength of 550 nm is not less than 50 % and is formed on a transparent substrate. Thereby, excellent photocatalytic action and optical transmissivity can be obtained. Moreover, members composing various

structures such as a glass window, which are especially required to have optical transmissivity, can further have photocatalytic activities. This respect is very important from the view of substantial enhancement of the light irradiation efficiency and the transparency.

Industrial Applicability

As above described, the titanium dioxide photocatalyst structure can be used as a member of various structures especially required to have the transparency, for example, a glass window. The present invention can have distinguished advantages in that actions of eliminating carbon dioxide and air pollutants (for example, NO_x and SO_x) from indoor space, of deodorizing the indoor space and of making the indoor space antibacterial, soil-resistant and mildew-proof are achieved by the window pane itself without using special equipment. Additionally, the present invention can obtain eminent merits in that in the case of cleaning the room by applying the photocatalyst structure to the window pane, sunlight can be extremely utilized. Moreover, especially, in the case of applying the photocatalyst structure of the present invention to a building or the like, in which glass materials are highly used, of the type that has become common in recent years,

the photocatalyst structure of the present invention has immeasurable advantages in cleaning the living space. In addition, the photocatalyst structure of the present invention can be applied to a glass door or the like of a shelf, which includes the door or the like, for storing, for instance, precision devices such as a camera which should be kept away from molds and corrosion. Furthermore, the photocatalyst structure of the present invention can be used for various purposes which require transparent glass. For example, the photocatalyst structure of the present invention can be applied to glass covers for various electronic equipment and instrument, light fixtures such as a fluorescent lamp and a light bulb, a lens and a glass. Thus, the range of application of the photocatalyst structure of the present invention is extremely wide.

* C L M S *

0 1 8 5 0 1 5

CLAIMS

1. A titanium dioxide photocatalyst structure comprising:

a titanium dioxide film which has at least photocatalytic activity and light transmittance corresponding to light having a wavelength of 550 nm is not less than 50 % and is formed on a transparent substrate.

2. The titanium dioxide photocatalyst structure according to claim 1, wherein the titanium dioxide film is 0.1 to 5 μ m in thickness.

3. The titanium dioxide photocatalyst structure according to claim 1 or 2, wherein the titanium dioxide film contains at least an anatase crystal.

4. The titanium dioxide photocatalyst structure according to claim 1, 2 or 3, wherein a precoat film having transparency is disposed between the transparent substrate and the titanium dioxide film.

5. The titanium dioxide photocatalyst structure according to claim 4, wherein the precoat film is 0.02 to 0.2 μ m in thickness.

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* C L M S *

6. The titanium dioxide photocatalyst structure according to claim 1, 2, 3, 4 or 5, wherein the transparent substrate is made of glass.

7. The titanium dioxide photocatalyst structure according to claim 4, 5 or 6, wherein the precoat film is made mainly of SiO_2.

8. A method for producing a titanium dioxide photocatalyst structure recited in claim 1, 2, 3, 4, 5,6 or 7, comprising a producing process which includes the step of:

forming a titanium dioxide film on a transparent substrate by performing a pyro-sol method, a dipping method, a printing method or a CVD method.

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ABSTRACT

A titanium dioxide film 2 having at least photocatalytic activity, whose light transmittance corresponding to light having a wavelength of 550 nm is not less than 50 % and thickness is 1 to 5 μ m or so, is formed on a transparent substrate 1 constituted by a glass plate or the like. Preferably, a precoat film 2, which has optical transmissivity and is constituted by a SiO_2 film having a thickness of 0.02 to 0.2 μ m or so, is provided between the transparent substrate 1 and the titanium dioxide film 2. Thereby, excellent photocatalytic action and optical transmissivity can be obtained. Moreover, members composing various structures such as a glass window, which are especially required to have optical transmissivity, can further have photocatalytic activities.

FIG. 1

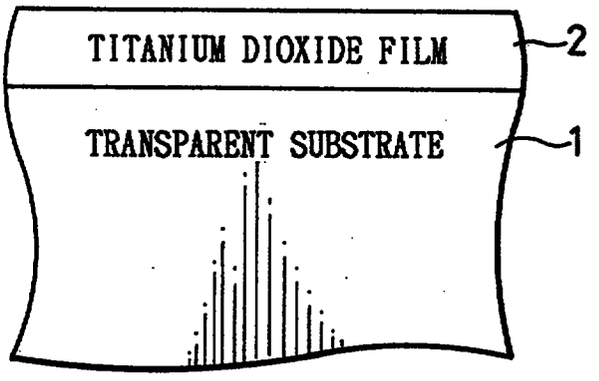

TITANIUM DIOXIDE FILM
2
TRANSPARENT SUBSTRATE
1

FIG. 2

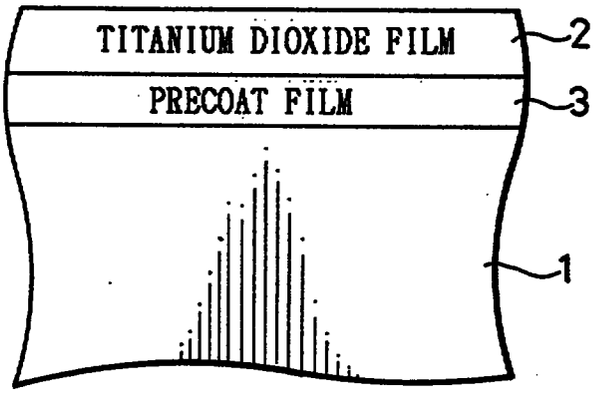

TITANIUM DIOXIDE FILM
2
PRECOAT FILM
3
1

FIG. 3

	TRANSPARENT SUBSTRATE	PRECOAT FILM COMPOSITION THICKNESS	TITANIUM DIOXIDE MEMBRANE	TRANSMITTANCE	DECOMPOSITION ACTIVITY
EXAMPLE		(μM)	(μm)	(%)	(μl/min)
1	SLG	NONE – – –	4.8	70	10.5
2	SLG	NONE – – –	0.3	75	0.15
3	SLG	NONE – – –	1.5	69	2.43
4	SLG	NONE – – –	2.3	80	8.10
5	SLG	NONE – – –	3.2	75	9.48
6	SLG	NONE – – –	4.1	70	10.8
7	SLG	SiO2 0.1	0.1	85	1.53
8	SLG	SiO2 0.1	0.6	91	5.87
9	SLG	SiO2 0.1	1.7	86	13.1
10	SLG	SiO2 0.1	2.3	77	14.5
11	SLG	SiO2 0.1	3.0	74	15.3
12	SLG	SiO2 0.1	4.2	72	15.6
13	QUARTZ	NONE – – –	0.5	86	13.2
14	QUARTZ	NONE – – –	2.3	60	14.4
15	SLG	NONE – – –	4.3	78	10.9
COMPARATIVE EXAMPLE					
1	SLG	NONE – – –	0.05	90	0.01 OR LESS
2	SLG	NONE – – –	4.3	70	0.01 OR LESS
3	SLG	NONE – – –	0.1g/50cm²	10 OR LESS	24.5

SLG:SODA LIME GLASS

FIG. 4

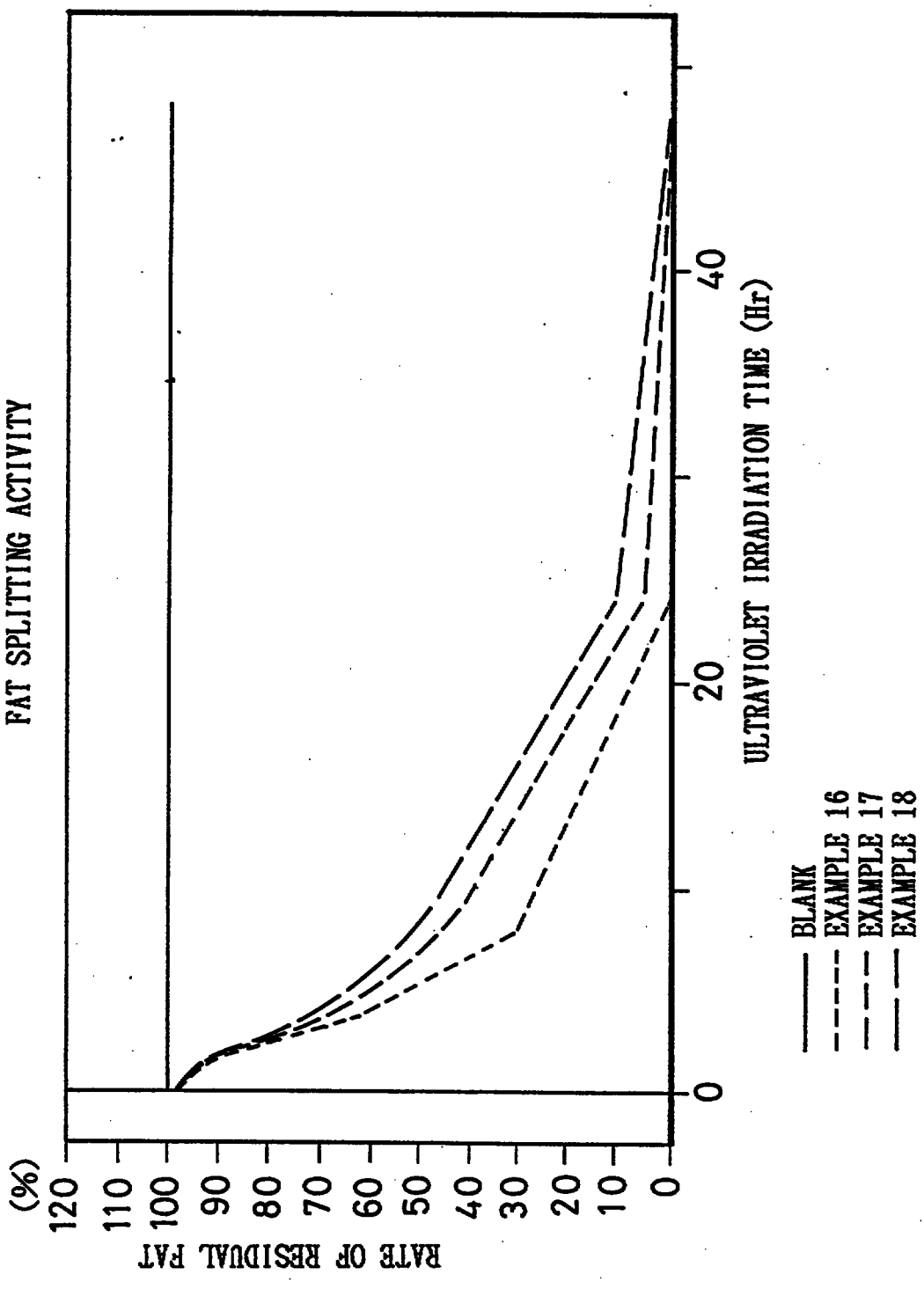
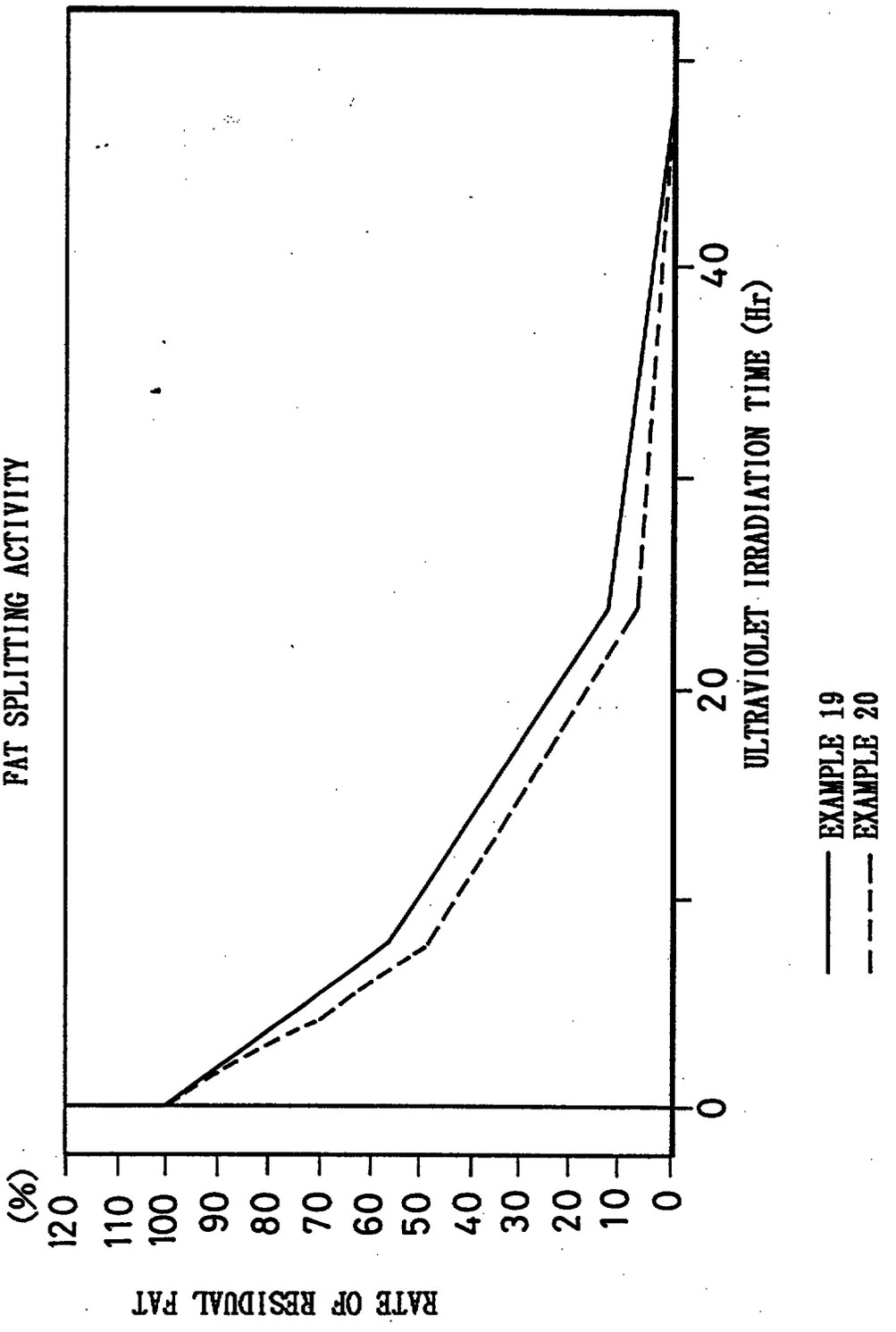

FAT SPLITTING ACTIVITY
RATE OF RESIDUAL FAT (%)
120
110
100
90
80
70
60
50
40
30
20
10
0
0
20
40
ULTRAVIOLET IRRADIATION TIME (Hr)
BLANK
EXAMPLE 16
EXAMPLE 17
EXAMPLE 18

FIG. 5


FAT SPLITTING ACTIVITY
RATE OF RESIDUAL FAT
(%)
120
110
100
90
80
70
60
50
40
30
20
10
0
0
20
40
ULTRAVIOLET IRRADIATION TIME (Hr)
EXAMPLE 19
EXAMPLE 20

* C L M S *

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CLAIMS

1 A titanium dioxide photocatalyst structure comprising:

a transparent glass substrate having first and second opposing surfaces, the first surface of said substrate receiving light from an external light source; and

a titanium dioxide film having first and second opposing surfaces, a light transmittance of said titanium dioxide film being at least 50 % for light having a wavelength of 550 nm, the first surface of said titanium dioxide film being formed on the second surface of said substrate, whereby light transmitted from said external source through the first and second opposing surfaces of said substrate and through the first surface of said titanium dioxide film to the second surface thereof causes photocatalytic action to be generated on the second surface of said titanium dioxide film.

2. The titanium dioxide photocatalyst structure according to claim 1, wherein said transparent glass substrate contains alkaline ingredients therein, and which further comprises a transparent precoat film interposed between the second surface of said substrate and the first surface of said titanium dioxide film.

3. The titanium dioxide photocatalyst structure according to claim 2, wherein said transparent precoat film has a thickness of 0.02 μm to 0.2 μm.

4. The titanium dioxide photocatalyst structure according to claim 3, wherein said precoat film is composed of SiO_2.

5. The titanium dioxide photocatalyst structure according to claim 1,

* C L M S *

wherein said titanium dioxide film has a thickness of 0.1 μm to 51 μm.

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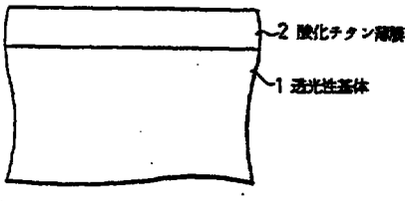
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(54) Title : TITANIUM OXIDE PHOTOCATALYST STRUCTURE AND METHOD OF MANUFACTURING THE SAME

(54) 発明の名称 酸化チタン光触媒構造体及びその製造方法



1 ... light-permeable substrate
2 ... titanium oxide film

(57) Abstract

It has been made possible to have a member provided with excellent photocatalytic effect and light-transmittivity, and, especially, constituting various kinds of structures, such as a window pane and the like, which demand transparency, provided also with a photocatalytic effect, by forming at least a titanium oxide film (2) of about 0.1-5 μm in thickness, which has a photocatalytic activity and not less than 50 % of linear transmittance with respect to the light of 550 nm wavelength, on a light-transmitting substrate (1) comprising a glass plate, and preferably providing a precoating film (2) comprising a light-transmitting SiO_2 film of around 0.02-0.2 μm in thickness between the light-transmitting substrate (1) and titanium oxide film (2).

（５７）要約

ガラス板等からなる透光性基体１上に少なくとも光触媒活性を有すると同時に波長５５０ｎｍの光に対する光直線透過率が５０％以上有する膜厚０．１～５μｍ程度の酸化チタン薄膜２を形成するとともに、好ましくは、透光性基体１と酸化チタン薄膜２との間に光透過性を有する膜厚０．０２～０．２μｍ程度のＳｉＯ$_2$薄膜等からなるプレコート薄膜２を設けることにより、優れた光触媒作用と光透過性を有し、しかも、特に透明性が要請されるガラス窓その他の種々の構造物を構成する部材に光触媒作用を兼ね備えさせることを可能にした。

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情報としての用途のみ
P.C.T.に基づいて公開される国際出願をパンフレット第一頁にPCT加盟国を同定するために使用されるコード

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