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Bezeichnung der Erfindung: Pigments and their preparation
Title of invention:
Titre de l'invention :

Klassifikation / Classification / Classement : C09C 1/36

ENTSCHEIDUNG / DECISION

vom / of / du 26 January 1989

Anmelder / Applicant / Demandeur :

Patentinhaber / Proprietor of the patent /
Titulaire du brevet : Tioxide Group PLC

Einsprechender / Opponent / Opposant : 01 Kronos Titan-GmbH
02 Bayer AG

Stichwort / Headword / Référence : Pigments/TIOXIDE

EPÜ / EPC / CBE Article 56

Schlagwort / Keyword / Mot clé : "Inventive step - improvement not foreseeable"

Leitsatz / Headnote / Sommaire

Case Number : T 42 /88 - 3.3.2

DECISION
of the Technical Board of Appeal 3.3.2
of 26 January 1989

Appellant : (Opponent 02)	Bayer AG, Leverkusen Konzernverwaltung RP Patentabteilung Bayerwerk D-5090 Leverkusen
Other party to the proceedings: (Opponent 01)	KRONOS TITAN-GmbH, Leverkusen Wissenschaftliche Abteilung - Patentgruppe - Postfach 10 07 20 Peschstrasse 5 D-5090 Leverkusen 1
Respondent : (Proprietor of the patent)	Tioxide Group PLC 10 Stratton Street London W1A 4XP GB
Representative :	Mercer, Christopher Paul Carpmaels & Ransford 43, Bloomsbury Square London WC1A 2RA GB
Decision under appeal :	Decision of Opposition Division of the European Patent Office dated 18 December 1987 rejecting the opposition filed against European patent No. 0 078 633 pursuant to Article 102(2) EPC.

Composition of the Board :

Chairman : P. Lançon
Members : A. Nuss
R. Schulte

Summary of Facts and Submissions

I. European patent No. 0 078 633 was granted on 5 February 1986 on the basis of seven claims, pursuant to European patent application 82 305 581.9 filed on 20 October 1982, which claimed the priority of an earlier application of 30 October 1981.

Independent Claims 1 and 5 read as follows:

"1. Titanium dioxide pigment comprising a core of particulate pigmentary rutile titanium dioxide having thereon:

an inner coating of dense amorphous silica in an amount of up to 12% by weight expressed as SiO_2 on weight of TiO_2

an intermediate coating of a hydrous oxide of zirconium in an amount of up to 5% by weight expressed as ZrO_2 on the weight of TiO_2 carried on said inner coating; and an outer coating containing a hydrous oxide of aluminium in an amount of up to 6% expressed as Al_2O_3 on weight of TiO_2 carried on said intermediate coating.

5. A process for the manufacture of a coated titanium dioxide pigment comprising:

depositing on a core of particulate rutile titanium dioxide from an aqueous solution of a water-soluble silicate at a pH greater than 8 an inner coating of a dense amorphous silica in an amount of up to 12% by weight when expressed as SiO_2 on weight of TiO_2;

treating the inner coating with a hydrous oxide of zirconium to form an intermediate coating on said inner coating in an amount of up to 5% by weight expressed as ZrO_2 on the weight of TiO_2; and

depositing hydrous alumina on said pigment after deposition of said hydrous oxide of zirconium in an amount of up to 6% by weight expressed as Al_2O_3 on weight of TiO_2 from a water soluble aluminium compound."

II. In a decision dated 18 December 1987, the Opposition Division rejected the opposition and maintained the patent unamended. The Opposition Division took the view that the invention as claimed was not only novel, but also involved an inventive step. The reasoning was essentially the following:

Document FR-A-2 177 059 (II) was identifed as the closest prior art and the technical problem vis-à-vis this document was considered to consist in improving the durability of the known coated pigments. Document DE-A-2 740 561 (VII) could not, however, lead to the solution of this problem for the reason that it followed from the table included on page 11 of document (II) that pigments coated with an inner layer of dense SiO_2 and an outer layer of Al_2O_3 had a lower degree of durability than those coated according to the process of document (II) with zirconium oxide on top of SiO_2, and that there thus existed no ground to suppose that in replacing in the latter the SiO_2 layer by a dense SiO_2 layer, the durability of the pigments could be further improved.

III. The Appellant (Opponent 02) filed a notice of appeal against this decision on 19 January 1988, paying the appeal fee at the same time. A Statement of Grounds of Appeal was filed on 26 March 1988.

IV. The parties having exchanged written submissions, oral proceedings took place on 26 January 1989 at the request of both parties. In the course of the present appeal proceedings, the parties expressed the following opinions:

(i) The Appellant's view is that in document (II) the pigment chosen for comparison does not have an inner coating of dense SiO_2 for the reason that precipitation of SiO_2 at a pH of 9 does not necessarily lead to a coating of dense SiO_2.

The improved durability shown in this prior document for pigments obtained in accordance with that invention is therefore to be considered as being solely the result of an additional zirconium oxide coating provided between the inner SiO_2 coating and the outer Al_2O_3 coating.

Since it is however known from document (VII) that good durability is due to an inner coating of dense SiO_2, it was obvious to expect even better results with an additional coating of zirconium oxide on top of the dense silica coating.

(ii) The Respondent stresses that in document (II) silica deposition is carried out at a pH between 1 and 3.5 in the presence of an acidic source of a soluble oxide of zirconium, hafnium or titanium. Under these conditions, however, what is precipitated on the pigment surface is not a layer of pure silica, but a mixed layer comprising both silica and zirconia, hafnia or titania. Moreover, the mixed layer will not be a dense layer, but a layer of ordinary, non-dense hydrous oxides.

As to the comparison, it is clearly stated in this prior document that the control (témoin) pigment itself has an extremely high durability and also that this titanium dioxide pigment is coated by use of a sodium silicate solution maintained at a pH of 9, which clearly signals to the man skilled in the art that the silica layer thus obtained is a dense amorphous silica layer, since it is known from document US-A-2 885 366 (III) that the only essential requirement for producing dense silica is to maintain the pH at above 8.

For the rest, document (VII) requires that an alumina layer be produced directly on top of a dense silica layer. The man skilled in the art had therefore no reason to combine this document with document (II).

V. The Appellant requested that the decision under appeal be set aside and the patent be revoked.

The Respondent requested that the appeal be dismissed and that the patent be maintained.

Reasons for the Decision

1. The appeal complies with the requirements of Article 106 to 108 and Rule 64 EPC and is, therefore, admissible.

2. The patent in suit relates to titanium dioxide pigments and to their preparation.

2.1 Document (II) is undoubtedly the closest prior art document. It discloses a process for the production of pigmentary titanium dioxide (preferably in the rutile form) comprising forming an aqueous suspension or slurry of particles of titanium dioxide containing a water soluble silicate, adding a water-soluble hydrolysable acidic compound of zirconium, hafnium or titanium and an alkali and/or alkali metal silicate, to maintain the pH of the suspension or slurry at a value of 1 to 3.5 during the addition of the compound and thereby precipitating a hydrous oxide of silicon on the particles, and subsequently raising the pH to effect complete precipitation of a hydrous oxide of zirconium, hafnium or titanium on the particles. However, addition of the acidic compound at a pH of from 1.0 to 3.5 not only leads to deposition of a hydrous oxide of silicon on the pigment particles, but at the same time precipitation of the hydrous oxide of the metal takes place. When the desired amount of hydrous oxide of silicon has been deposited, the pH is raised to effect complete precipitation of the hydrous oxide of zirconium, hafnium or titanium. The amount of hydrous oxide of silicon applied (expressed as SiO_2) is usually below 20% of the weight of TiO_2. Optionally a further coating of a hydrous oxide of aluminium, titanium, cerium, zinc, zirconium or silicon can be applied (up to 10% by weight, as the oxide, on TiO_2) (see Claim 1; page 1, lines 23/24; page 3, lines 5 to 14, lines 17 to 19 and lines 26 to 30 and page 4, lines 4 to 6).

It is further stated on page 11 of this document that the results shown in the "Table" disclosed on the same page "clearly show the superiority of the pigments prepared according to the Examples in so far as durability ... is concerned" (see lines 22/23). In this table, the pigments described in the example were compared with a control ("témoin") pigment known to have an extremely high durability. This control pigment had been prepared by coating titanium dioxide by adding to an aqueous suspension of the pigment sodium silicate solution simultaneously with a dilute acid to maintain the pH of the suspension at 9 followed by the application of an outer coating of hydrous alumina (see page 10, lines 28 to 34 of document (II)).

2.2 As stated in the patent in suit, titanium dioxide pigments, particularly rutile titanium dioxide pigments, are valuable materials for use in pigmenting a wide variety of products including paints, which in use are required to exhibit a high degree of so-called durability in withstanding degradation of the product by the action of light. There is a desire always for improvements in pigments and paint media to increase the durability and to extend the effective life of the products (see col. 1, lines 5 to 14).

3. The technical problem in respect of the closest prior art consisted thus in further improving the durability of titanium dioxide pigments in the rutile form.

In order to solve this problem, it is proposed according to Claim 1 of the patent in suit, to provide a pigment of the known type with:

(i) an inner coating of dense amorphous silica in an amount of up to 12% by weight expressed as SiO_2 on weight of TiO_2;

(ii) an intermediate coating of a hydrous oxide of zirconium in an amount of up to 5% by weight expressed as ZrO_2 on the weight of TiO_2 carried on said inner coating;

(iii) an outer coating containing a hydrous oxide of aluminium in an amount of up to 6% expressed as Al_2O_3 on weight of TiO_2 carried on said intermediate coating.

In view of the results given in Table 2 of the patent in suit (see col. 14, lines 1 to 20), the problem is indeed solved by the claimed pigment. The same remark also applies to the "adjusted" results given in Table A filed together with Respondent's letter dated 15.4.87, in which the durability ratios indicated in the patent in suit had been adjusted in order to provide results which could be directly compared to those known from page 11 of document (II). This was not in dispute.

4. In the absence of any document which discloses all the features of the claimed pigment, the subject-matter of Claim 1 of the patent in suit is new. This was not disputed by the Appellant.

5. It remains, therefore, to be examined whether the requirement for inventive step is met by the claimed solution to the technical problem as indicated in paragraph 3 above.

5.1 The Appellant did not contest that the claimed pigments showed substantially improved durability when compared to a pigment obtained according to document (II). He did contend, however, that it was obvious for a man skilled in the art to expect this better result, since it appeared from document (VII) that good durability was due to an inner coating of dense SiO_2 and from document (II) that the pigment chosen for comparison did not have an inner coating of dense SiO_2 in view of the precipitation of SiO_2 at a pH of 9, whereby the improvement could thus obviously be solely the result of an additional zirconium oxide coating provided on top of the inner non-dense SiO_2 coating before applying an outer coating of hydrous alumina.

5.2 The Board is however neither convinced that in document (II) the control (témoin) pigment does not possess a dense SiO_2 coating, nor that for the man skilled in the art the claimed solution was foreseeable.

5.2.1 The process of preparing the control pigment mentioned in document (II) differs from that described in document (VII) mainly in that no indication concerning the working temperature and the cure time is given. As stated in the latter, to achieve an impervious silica coating it is essential that the silica stays in contact with the titania at a pH between 9 and 10.5 for at least 15 minutes. The exact curing time will be however dependent on the pH and temperature of the system, whereby at a temperature of 80°C and pH of 9 cure time will be 60 minutes compared with 15 minutes at a temperature of 100°C and pH of 10.5. This means that, in general, the lower temperature the higher the pH required (see Claim 4; page 6, paragraph 3 and page 11, Example 1).

The Board is not convinced that the man skilled in the art would infer from this teaching that working at temperature below 80°C, or without any heating at all, silica would not deposit as a dense coating, since it is not only known from document (III) that at a pH between 8 and 11 a skin of dense, amorphous silica may be obtained on a core like titanium dioxide at a temperatures between 60°C and 80°C, but also that below 60°C the real difficulty is actually to bring about the formation of a (silica) skin <u>at a practical rate</u>, since silica can be formed into a skin more readily at a higher temperature (the relation between time and temperature may be roughly estimated from the observation that within the range from 60°C to 125°C the reaction rate doubles for about every 10°C rise in temperature) (see col. 3, line 22; col. 4, lines 31 to 33; col. 8 lines 16 to 58).

In view of this relationship between reaction time and temperature, and in the absence of evidence to the contrary, the Board considers it very likely that the control pigment used in document (II) was coated with a dense amorphous skin of silica, although it is admitted that no heating is mentioned in this document and that without heating the reaction time must be expected to be long. This was however not the point at issue.

Furthermore, regardless of the fact that the information contained in document (III) manifestly weakens the Appellant's allegation concerning the nature of the SiO_2 coating, it is in no way sufficient in opposition proceedings for the Opponent to call in question a granted patent with an unsubstantiated assertion (cf. decision T 219/83, "Zeolites/BASF", OJ EPO 7/1986, 211-226, in particular point 12 of the Reasons for the Decision).

5.2.2 It is true that according to document (VII), the dense, amorphous silica coating is considered to be primarily responsible for the durability of the finished titanium dioxide (see page 7, penultimate paragraph). But the man skilled in the art knew in addition from document (II) that an improvement over such coated pigment - known to have extremely high durability - had been achieved by coating TiO_2 in quite a different way, whereby an (inner) coating of ordinary, non-dense hydrous oxide of silicon was obtained, on top of which a hydrous oxide of zirconium, hafnium or titanium was deposited before coating the pigment with an outer coating of hydrous alumina. However, the inner coating was not of pure silica, but a coating comprising necessarily also the hydrous oxide of the metal zirconia, hafnia or titania (see point 2.1 above). It is not explained in document (II) why increased durability had been obtained over the control pigment.

The pigment obtained in document (II) differs from that in document (VII) thus not only by the different physical form of the silica coating, but also by the quite different composition of the inner coating as well as the additional intermediate coating of hydrous metallic oxide. The superior durability of the former can therefore only be seen as the result of these differences together or in other words, as the result of a fundamentally different type of coating when compared to the previous coating with dense silica.

It follows from all this that when trying to further improve durability the man skilled in the art had obviously no reason at all to suppose that the key to this consisted in a twofold modification of the inner coating of the pigment described in document (II) and in choosing, at the same time, from the three possible hydrous metal oxides for the intermediate coating just the zirconium compound.

Moreover, in document (II) there is a continuous deposit of hydrous oxide of zirconium when coating TiO_2, first concomitantly with silica deposition (inner coating) and at the end in pure form (intermediate coating). Although this is an essential feature of that invention, it must be pointed out again that it is nowhere explained in this prior art document where the superiority of these pigments over those with an inner coating of dense silica (control pigment) comes from and the Appellant has failed to give any reason why the man skilled in the art would have considered that in this tandem structure containing necessarily hydrous oxide of zirconium throughout both coatings, durability was essentially conferred by the coating containing also silica with the pure hydrous oxide of zirconium on top of this coating merely enhancing the effect, such an assumption being a prerequisite for taking into account replacement of the inner coating.

5.2.3 It follows from the above that the man skilled in the art had obviously no reason to replace in the pigment described in document (II) the inner mixed coating by a coating of dense, amorphous silica in order to further improve durability of the pigment.

The subject-matter of Claim 1 as well as that of Claim 5 is therefore based on an inventive step.

Since dependent Claims 2 to 4 and 5 to 7 concern particular embodiments of the claimed product and the process for manufacturing it, they too are allowable.

Consequently, there are no grounds which prejudice the maintenance of the patent.

Order

For these reasons, it is decided that:

The appeal is dismissed.

The Registrar: The Chairman:

F.Klein P.Lançon