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EXPERIMENTAL STATION
RESEARCH AND DEVELOPMENT DIVISION TECHNICAL REPORT
CHEMICALS, DYES & PIGMENTS DEPARTMENT
E. I. DU PONT DE NEMOURS & COMPANY

DENSE ALUMINA COATINGS ON TITANIUM DIOXIDE PIGMENTS

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ABSTRACT

A dense alumina coating on titanium dioxide pigment performs as a barrier to UV induced chalk-fade reactions. As little as 2% dense alumina coating exhibits durability equivalent to R-960, our most durable pigment (6% SiO_2, 2% Al_2O_3 coating) in chemical sensitivity testing. Dense alumina coatings are under study as a means of producing a single grade slurry pigment (high gloss/durable). Chemical systems and processing conditions have been defined for producing dense alumina coatings for consolidating durable grade R-902 and high gloss grade R-900 into a single product.

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INTRODUCTION

Du Pont currently achieves durability (resistance to UV induced chalk-fade reactions) with titanium dioxide pigments by coating the particulate TiO_2 with dense amorphous silica. The silica coated pigments require a second coating of hydrous alumina to optimize the dispersion of the product. Du Pont markets two pigments for the coatings industry that have the silica-alumina combination treatments, namely R-960 (6% SiO_2, 2% Al_2O_3) and R-902 (1.5% SiO_2, 3.0% Al_2O_3). These products have given problems over the years in achieving a high gloss coating. The difficulty has been attributed to the presence of silica. Further, if legislative action against the presence of silica on titanium dioxide pigments would come to pass, a new method of achieving durability would be required.

We are exploring the use of dense alumina coatings as a means of producing a durable titanium dioxide pigment. La Porte Industries markets a durable pigment product, RO-676, that has been characterized to be rutile titania pigment with a 5% dense alumina coating. Our evaluation of their product, RO-676, reveals that the pigment has chalk-fade resistance intermediate to R-960, our most durable pigment, and R-902, our 1.5% silica coated product.

OBJECTIVES

Studies with the dense alumina coatings are being carried out to define a practical, non-silica procedure for producing a durable pigment. Since the coating will be silica-free, an opportunity exists to improve the gloss of the durable pigment. A thorough understanding of the chemistry involved in obtaining a dense alumina coating on titanium dioxide, could simplify the method and reduce the amounts of coating necessary for goal durability.

One of the goals of our product development work is to consolidate two of our slurry grade pigments into a single grade. If the gloss of a durable pigment such as R-902 can be increased by 10-12 points, a single trade sales coating slurry exhibiting high gloss and durability could replace the two grades currently marketed. Our studies with dense alumina coatings are directed at durability with improved gloss, with consolidation of grades as a goal.

SUMMARY AND CONCLUSIONS

A dense alumina coating on titanium dioxide pigments performs as a barrier to UV induced chalk-fade reactions.

Several routes to achieve a dense alumina coating by blend tank procedures have been described. Chemistry to generate the coating in SDG processing has been demonstrated in simulated SDG experiments.

A 2% dense alumina coating on rutile pigment exhibits chemical sensitivity values (graying) equivalent to or better than R-960, our most durable pigment.

The most critical parameter in applying the dense alumina coating for durability is the pH of the system. The lower the pH, in the 3-7 range, the more durable the coating. The lower pH's cause sulfate to be retained in the coating which apparently contributes to durability. The optimum pH for durability and gloss appears to be bracketed between 7 and 8.

PATENT SITUATION

Patent Protection

Du Pont has no patents on dense alumina coatings for durability. R-960 and R-902 are covered by Werner U. S. P. 3,437,502 (reissue 27818).

Filing Action

A patent proposal will be prepared in 2Q'80 when the work is better defined. Patent opportunities look promising on this type of product.

Domination Status

A search will be requested when potential products and processes are defined. British Patent 1,336,292 to La Porte appears to describe the method used to generate dense alumina on their product, RO-676. No U. S. counterpart has been found.

PROGRAM

This program has been active for approximately six months. We have demonstrated goal durability with dense alumina coatings and have under study, preparations of sufficient quantities of pigment to measure gloss. The goal product is one with R-900 (08) gloss and R-902 durability. We will carry out studies in blend tanks to determine if such a product is feasible with dense alumina coatings. It is anticipated that an answer to that question should be available in the 4th quarter of 1979.

Long range, we plan to apply the dense alumina coating via SDG processing. Laboratory SDG simulation experiments should be concluded by the end of the third quarter 1979. An SDG plant scale run will be tried if laboratory simulations are encouraging.

PUBLICATION STATUS

There are no plans to publish any portions of this program.

SPECIAL SAFETY PRECAUTIONS

The product formed is not toxic. The chemicals used to treat the pigment are handled in accordance with normal practices. However, in situations wherein the pigment gets airborne, dust masks and hoods are used. Gloves are worn for all chemical handling.

ENVIRONMENTAL CONSIDERATIONS

There are no pollution problems associated with this work that would not be considered normal in our pigment processing systems, in the laboratory or plant.

ACKNOWLEDGEMENT

The writer gratefully acknowledges the assistance of William Stephens and Tom Stecher for the experimental work. Analytical assistance by E. N. Buckley, C. V. Miller, T. S. Buckley, G. R. Wilbur, and W. J. Eissing is acknowledged.

R. DeColibus has contributed to this program via discussion, sample preparation, and evaluation.

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DISCUSSION AND EXPERIMENTAL

A. Evaluation of Durable Pigments

A durable titania pigment is one in which UV chalk-fade reactions have been minimized by special surface treatments. Our standard silica coated pigment products are evaluated for durability by:

1. Acid Solubility - Product is subjected to sulfuric acid under controlled temperature and concentration to determine how effectively the titania pigment has been coated. The test is described in TP-109.2.

2. Accelerated Chalk-Fade Test - Pigment is evaluated by measuring the change in red reflectance as a function of hours exposure in a weatherometer, an instrument with controlled humidity and UV radiation. The pigment is incorporated in Auto Refinish Syntex 3833 with a Ramapo Blue Tint.

3. Florida Chalk-Fade Evaluations - Pigment is evaluated by measuring the change in red reflectance as a function of exposure time in Florida. The pigment is incorporated in Auto Refinish Syntex 3833 with a Ramapo Blue Tint. The red reflectance varies directly with the amount of chalk. The procedure described by W. H. Daiger and W. H. Madson, E. I. du Pont (Chalk-Fade Evaluations of Pigmented Finishes by Use of Instrumentation and Computer Analysis) - is used for the actual chalk-fade values. This test is the most critical of all durability evaluations.

4. Chemical Sensitivity (TP-417-2) - In this test, pigment is slurried with glycerine and basic carbonate of white lead, sealed between glass slides and subjected to UV radiation. Highly UV active pigments cause formation of elemental lead. The blackness/grayness is determined by comparing to standards.

Tests 2, 3, and 4 can be used to evaluate dense alumina pigments. Test 1 cannot be used since the dense alumina coating itself is soluble in H_2SO_4.

B. Characterization of LaPorte's Dense Alumina Coated Product RO-676

The commercial La Porte pigment product, RO-676, received August, 1977, and designated as TC-8729 has the characterization values shown below.

TC-8729 - Composition (coating)

5.6% Al_2O_3

2.0% sulphate

1.2% hydrous TiO_2

0.0% silica

0.02% carbon

Paint Properties

30 J Gloss = 68

TFW 153.1 = 7-3(M)

pH of pigment = 4.9

Durability

Pigment	Coating	C-F Rating (Florida)	Chemical Stability (Graying)
R-902 (Du Pont)	1.5% SiO_2/3% Al_2O_3	20	3.5
RO-676 (La Porte)	5% dense Al_2O_3	28	2.0
R-960 (Du Pont)	6% SiO_2/2% Al_2O_3	35	2.0

C. Samples Prepared with La Porte's Patent Teaching

Using the preferred case of La Porte's British Patent 1,336,292 as well as a variation with new chemistry, two sets of samples were prepared with a nominal 5% dense alumina for evaluation in emulsion gloss, 30 J gloss, graying, accelerated chalk-fade and Florida exposure. Some variations in micronizer additives were used on the finished pigments to attempt to optimize gloss.

TABLE I

SAMPLE #	COATING	MICRONIZER ADDITIVE	IG-90-2 60° Gloss	IG-90-2 R.H.	30J GLOSS	GRAYING
E-17878-105A	5% Al_2O_3-La Porte	-	38	100	67	2.5
E-17878-105B	"	0.3% TEA	45	104	75	2.5
E-17878-105C	"	0.5% TEAAL	49	106	73	2.5
E-17878-106A	5% Al_2O_3-Chlorhydrol®	0.3% TEA	59	102	58	3.0
E-17878-106B	"	0.5% TEAAL	56	100	64	3.0
Controls						
R-960						2.0
R-940(08) Standard			75	100		7.0
R-940(28) Standard			64	100		7.0
R-942	JV Data (1st Quarter Average)		57.4 (range 41-64)			3.5

Notebook E-17878 -105-106-107-110-111-115-125

Five percent dense alumina can be applied to TiO_2 by La Porte's patent teachings or with variations that give gloss values in emulsion paint systems and alkyd systems (30J) that are similar to our R-942 system. R-942 is a durable slurry prepared from R-902 (1.5% SiO_2, 3.0% Al_2O_3). The durability (graying) is somewhat better than R-942. Accelerated chalk-fade and Florida exposures on these pigments gives additional durability data when values are received. It appears that less than 5% Al_2O_3 would give R-902 durability and would probably result in an increase in gloss. Our experimental program to determine the level of dense alumina to give R-902 durability is discussed in the next section.

D. Blend Tank Systems for Dense Alumina

Blend tank type treatmentswere carried out to establish the level of dense alumina required to get R-902 (1.5% SiO_2, 3% Al_2O_3) durability. The laboratory chemical sensitivity test was used to measure the graying of the experimentals versus R-902.

Two different chemical systems were used:

(1) $Al_2(SO_4)_3 + NaOH$

(2) $Al_2(OH)_5Cl + H_2SO_4$

The treatments were applied by blending the ingredients with 400 g/l slurry of R-900 cyclone discharge. The pH was raised to 7 and held during ingredient addition. The samples were then washed free of salt, filtered, and dried for the chemical sensitivity test.

The data from the two systems for achieving dense alumina agrees quite well. Dense alumina coatings are extremely effective in gaining low chemical sensitivity for titanium dioxide pigments. Two percent dense alumina coating can be applied to get the chemical sensitivity of R-960 (6% SiO_2, 2% Al_2O_3),our most durable pigment.

TABLE II

$Al_2(SO_4)_3$ + NaOH at pH=7

Theoretical Al_2O_3 Coating (%)	Chemical Sensitivity (Graying)
8	1.5
6	1.5
4	1.5
2	2.0
1	4.0
Controls R960	2.0
R902	3.5

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TABLE III

$Al_2(OH)_5Cl$ + H_2SO_4 at pH=7

Theoretical Al_2O_3 Coating (%)	Chemical Sensitivity (Graying)
8	1.0
6	1.0
4	1.5
2	2.0
1	4.0
Controls R960	2.0
R902	3.5

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E. Blend Tank Systems and Processing Variations

In section (D) it was shown that 2% dense alumina gave goal durability when evaluated by the chemical sensitivity test. We then explored different coating conditions with a number of chemical systems for dense alumina in order to find the optimum system and conditions for durability.

Chemical Systems

$Al_2(SO_4)_3/NaOH$; $Al_2(SO_4)_3/NH_4OH$; $NaAlO_2/H_2SO_4$;

Chlorhydrol®$[Al_2(OH)_5Cl]/H_2SO_4$; and $Al_2(OH)_5Cl/(NH_4)_2SO_4$

In these experiments the TiO_2 is treated with the different dense alumina precursors at a variety of pH conditions. In all cases the theoretical alumina level was 2%. After the coating reactions, the pigment was washed salt free, filtered, dried, and characterized for durability by the chemical sensitivity test.

The studies were carried out on 400 g/l TiO_2 slurries in which 50 gram samples of pigment were used.

The data in Tables IV and V show that the best durability values are achieved if the dense alumina coating is finished between pH = 6-8. It further reveals that a 60°C thermal treatment in the blend tank enhances durability. There are many options in selecting precursors for dense alumina coatings. Processing conditions with these various precursors are critical.

F. Chemical Systems for Dense Alumina via Simulated SDG Processing

In these systems, the salt product of neutralization must be volatile. The alumina precursor chosen was Chlorhydrol®, the source of sulfate $(NH_4)_2SO_4$ and the base for neutralization, NH_4OH. The TiO_2 was slurried with the chemical ingredients for dense alumina. The slurry was filtered and subjected to a 400°C heat treatment to eliminate the NH_4Cl. The resulting pigment was evaluated in the graying test. Table VI summarizes the two simulated SDG runs.

The simulated SDG runs exhibit excellent graying values, well within goal. The 400°C thermal treatment for volatile salt expulsion is much higher than can be reached in SDG processing. In actual SDG processing the temperature for expelling the volatile salts would be near 150°C. The efficiency of salt removal in this processing, however, should be excellent. The temperature of SDG processing should be very effective in densifying the alumina coating.

Nominal six pound batches of pigment will be prepared via simulated SDG processing to evaluate gloss and other paint properties. When simulated SDG processing achieves goal properties, a plant scale run will be made.

Table IV

Dense Al_2O_3 Coating - Theoretical 2%

pH TiO_2/distilled H_2O	Additives	Final pH	Graying
4.2	$Al_2(OH)_5Cl + H_2SO_4$	1.8	8
4.2	$Al_2(OH)_5Cl + TiCl_4 + H_2SO_4$	1.0	8
4.2	$Al_2(OH)_5Cl + TiCl_4 + H_2SO_4 + NH_4OH$	7.0	2
4.0	$Al_2(SO_4)_3 \cdot (NH_4)_2SO_4 + NH_4OH$	7.0	4
3.7	$Al_2(SO_4)_3 + NH_4OH$	7.0	6
3.7	$Al_2(SO_4)_3 + TiCl_4 + NH_4OH$	7.0	4
3.5	$Al_2(OH)_5Cl - H_2SO_4 - NaOH$	7.0	2
3.5	$Al_2(OH)_5Cl - H_2SO_4 - NaOH$	8.0	2
3.5	$Al_2(OH)_5Cl - H_2SO_4 - NaOH$	9.0	3.5
3.5	$Al_2(OH)_5Cl - H_2SO_4 - NaOH$	9.5	7.0
3.5	$NaAlO_2 - H_2SO_4$	6.0	3.5
3.5	$NaAlO_2 - H_2SO_4$	8.0	7.0
3.5	$Al_2(SO_4)_3 + NaOH$	7.0	2.0
3.5	$Al_2(SO_4)_3 + NaOH$	8.0	3.0
3.5	$Al_2(SO_4)_3 + NaOH$	9.0	4.0

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Table V

Dense Al_2O_3 Coatings - Theoretical 2% (R. DeColibus)

pH TiO_2/distilled H_2O/H_2SO_4	Additives	pH	Graying
1.0	H_2SO_4 + $NaAlO_2$	4.0	2
1.0	H_2SO_4 + $NaAlO_2$	5.5	2
1.0	H_2SO_4 + $NaAlO_2$	8.0	3
1.0	H_2SO_4 + $NaAlO_2$	7.0	2

TiO_2/distilled $H_2O/H_2SO_4/Al_2(OH)_5$ Cl	Additives *	pH	Graying
1.0	NA_2SO_4/NaOH	8.0	1.0
1.0	NA_2SO_4/NaOH	7.0	1.0
1.0	NaOH only	8.0	1.0

* cured at 60°C

TABLE VI

Dense Al_2O_3 Coatings on TiO_2 (Simulated SDG)

Initial pH	Additives	Final pH	Temp for Salt Removal	Graying
3.7	$Al_2(OH)_5Cl + (NH_4)_2SO_4 + NH_4OH$	7	400°C	1
3.7	$Al_2(OH)_5Cl + TiCl_4 + (NH_4)_2SO_4 + NH_4OH$	7	400°C	3

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Appendix

Materials Used

Chlorhydrol® - Reheis Co.

$Al_2(SO_4)_3 \cdot 18H_2O$ Fisher Scientific

$NaAlO_2$ - Matheson, Coleman and Bell

$TiCl_4$ - Fisher Scientific

NaOH - Fisher Scientific

Triethanolamine - Fisher Scientific

Aluminum IsoPropoxide - Chattem Chemical Co.

H_2SO_4 - Fisher Scientific

$(NH_4)_2SO_4$ Fisher Scientific

NH_4OH Fisher Scientific

TiO_2 Pigment - Johnsonville Line I (Cyclone discharge)

Glossary

TEA - Triethanolamine

TEAAL - Triethanolamine Aluminate

Chlorhydrol® - $Al_2(OH)_5Cl$

Dense Alumina Coating - A hydrous alumina coating prepared in presence of sulfate

SDG - Processing unit for Simultaneously Drying and Grinding pigment

Indexing Terms

Durable Pigment coatings

Dense Alumina coatings

Blend tank coatings

Simulated SDG coatings

Consolidation of Grades

PIGMENTS DEPARTMENT

WHITE PIGMENTS

APPROVED LABORATORY METHOD

"TI-PURE" TESTING

CHEMICAL SENSITIVITY

DATE: October 3, 1947. This issue of the method supersedes the last dated July 17, 1944.

APPLICATION: The chemical sensitivity test was developed for use in determining the cut-off point at the kiln in the manufacture of antimony-treated pigments.

HISTORY: This test was developed at Baltimore used there in conjunction with "TI-PURE" Y grade production. It was revised at the request of Edge Moor Control to include more exact testing procedure, and issued under date of 7/17/44. It is now reissued in standard form for inclusion in the laboratory manuals.

PRINCIPLE: The antimony treatment of certain "TI-PURE" grades acts as an inhibitor in preventing reduction of a paste prepared with white lead, "TI-PURE" and glycerine. This reduction is evidenced by a darkening (formation of metallic lead) of the paste film on exposure to ultraviolet light.

EQUIPMENT:

Basic carbonate of white lead, W-11
Glycerine, Baker's C.P.
Sun lamp, type S-1
Clean glass plates, 4" x 6"
Standard pigments, at 0 and 10 chemical sensitivity rating. Refer to Manual Codes, TP-817.1 and TP-818.1 or revisions thereof.

PROCEDURE: 1. Grind LL samples prior to testing, either by mortar and pestle or by dry ball milling.

2. Weigh 2.5 grams of basic carbonate of white lead and 0.5 grams of each standard and of the ground pigment sample to be tested, and transfer each mixture to a clean color plate. General cleanliness is important throughout the test because contamination by foreign agents can readily affect the result.

3. To each pigment mixture on the plate add 0.75 ml. of glycerine, and rub into pastes with a small glass muller in the same manner as when rubbing a paste for color determination.

4. Set each paste aside as it is made up and cover with an inverted can or similar object so as to protect it from the light while the next paste is being prepared. Prepare a fresh set of standard pastes for each sample being tested.

5. Make drawdowns on a glass plate (4" x 6" texture slide) with the sample paste between the two standard pastes. Make the drawdowns lengthwise with each paste about 3/4" wide and 2" long.

6. Expose the pastes through the glass to a sun lamp at a distance of 14 inches from the light source for a period of 5 minutes.

7. Grade the sample paste promptly as soon as exposure time is completed and through the glass. It will be seen that the 10 standard will be light in color and the 0 standard will be dark. Rate the sample between the standards as to degree of darkening, and report the result as a whole number.

NOTES: 1. It has been found that these pastes cannot be retained for any length of time. Therefore, each sample is tested singly and completely with its own set of standards prepared at the same time.

2. Two standards must always be used for grading chemical sensitivity.

3. The drawndown film on the glass slide must be thick enough to prevent the passage of light.

4. A chemical sensitivity of 10, or no color change, indicates properly treated material. When this material is delivered from the kiln, a cut-off is usually made.

The same test is used for cutting off from "Y" to another grade material, the cut-off usually being made at a chemical sensitivity of 5.

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