KN-63-1 FLAKE PIGMENT SCOUTING By: H. R. Linton 1/60-7/62

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PIGMENT COLOR RESEARCH REPORT

FLAKE PIGMENTS SCOUTING

Period Covered January, 1960 - July, 1962 - Part Time

FILE: 210.8

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NJ 22608

DUP050054526

GR 425416

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KN-63-1

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

SUBJECT: FLAKE PIGMENT SCOUTING

PERIOD COVERED: January, 1960 - July, 1962 - Part Time

H. R. Linton

PREPARED BY: H. R. LINTON DATE SUBMITTED: 1/7/63

B. H. Perkins

SUBMITTED BY: B. H. PERKINS DATE RELEASED: 1/9/63

DUP050054527

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INTRODUCTION

For years there has been a demand for a durable, non-toxic, lot cost pearlescent pigment of general utility to give desirable decorative effects.

This report covers the laboratory work that has resulted in a new family of nacreous flake pigments ("Afflair"* pigments) which can be marketed in a dry, easily dispersible form, have excellent lightfastness, and are generally non-toxic, relatively low in cost and give outstandingly attractive color effects.

SUMMARY AND CONCLUSIONS

A range of nacreous flake pigments, colored by interference effects, has been made in the laboratory by hydrolysis of titanium dioxide on the surface of a flake substrate. The resulting flakes can be varied in hue from a silver-blue through a silver, gold, red, violet, blue and finally a green by controlling the thickness of the titanium dioxide film deposited. The flake body color may also be varied by incorporation of various ions in this titanium dioxide layer. The flakes made by hydrolysis of titanium dioxide on mica flakes have outstanding light and chemical stability after calcination (950°C.), and need only mild mixing to insure dispersion in paints, plastics, inks, etc.

The DuPont Company is presently marketing NF-104-D a pearl flake and NF-103-D a gold pearl flake. Plans to market several other flake products are now being developed.

REFERENCES: General: N.B. 1642, 1666, 1685, 1701, 1724

PATENT STATUS

Patent proposals have been prepared and filed.

(1) New Nacreous Pigments (Case 1457K)

(2) New Colored Flake Pigments (Case 1473K)

DISCUSSION AND BACKGROUND

Considerable information is available in the literature concerning the properties of natural pearl essence (guanine). The crystals of guanine obtained from fish vary considerably in size from 0.1 to 0.02 by 0.001 millimeters to only 2 to ten microns in length. The crystals are extremely brilliant flat blades and appear not unlike highly polished silver. The refractive indices recorded in the literature are $\alpha = 1.45$, $\beta = 1.8$, and $\gamma = 1.85$. When these flakes are suspended in a light transmitting film-forming vehicle ($n = 1.5$-1.6) the thin plate-like crystals lie parallel to one another and generally also parallel to the vehicle surface so that

the simultaneous reflection of light from the many surfaces at different depths produce the velvety pearl-like luster. One concludes from the physical characteristics of natural guanine that the requirements for a material to be pearlescent are (1) transparency, (2) flake-like shape, and (3) a high index of refraction.

A considerable number of inorganic substances have been examined as possible substitutes for the natural compound. As far as inorganic substances other than metal powder are concerned, it appears that salts of heavy metals such as lead, bismuth, silver, mercury, or thallium are required to obtain sufficiently high indices of refraction.

As far as is known, no organic substitutes for pearl essence are used in industry. The problems of selecting organic compounds for trial is difficult inasmuch as not much information regarding the refractive indices of solids organic compounds is available in the literature. A large number of organic compounds are described in the literature as crystallizing in the form of glistening or pearly scales.

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TABLE I

Compounds	Comment
Bismuth oxychloride	poor lightfastness
" oxynitrate	" "
" oxycarbonate	" "
" phosphate	not nacreous
" oxybromide	" "
Antimony "	" "
" oxychloride	" "
Tin phosphide	" "
Chromium nitride	" " - colored
Aluminum "	" "
Cadmium ammonium phosphate	" "
Barium " "	" "
Synthetic micas	Low refractive index
Glass flakes (n = 1.97)	weakly nacreous
Boron nitride	" "
Titanium sulfide - titania	" "
" carbide - "	" "
Stannic sulfide - Tin dioxide	" "
Zirconium " - Zirconia	" "
Barium titanate	not nacreous
Heated natural mica	nacreous only in large particle size
Oxanilide	low refractive index
5,6-dihydro-11,12-diketo-5,6-diazonaphthancene	" " "
Dibenzoyl benzene	" " "
Benzimidazolone	" " "
Dimethylcarbazole	soluble
Diacetyldiphenyl ether	low refractive index
Chlorocarbazole	soluble
Bromocarbazole	"
Indolo-2,3-carbazole	not nacreous
3-aminocarbazole	soluble
3,6-diamonocarbazole	not nacreous

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SUMMARY OF EXPERIMENTAL DETAILS

A. General

Several inorganic compounds having plate-like character were prepared and evaluated. The compounds included: boron nitride, sulfides of titanium, tin, and zirconium, which were converted to the oxides, bismuth salts such as oxynitrate, oxychloride, and oxycarbonate, various metal ammonium phosphates and several synthetic micas. Although the lustrous effect produced by some of these compounds was rather pronounced, all the samples were eliminated as pigment candidates for one or more outstanding reasons.

Several organic compounds were prepared or procured and evaluated. In most cases, the compounds were too soluble in solvents, a few gave lustrous effects but were very much inferior to the known pearl pigments. The Inorganic and organic compounds examined are listed in Table I.

The research program now turned to coatings.

B. Substrates

Mica, which possesses a lamellar plate-like structure, is very inert and has a low refractive index, was shown to be the best substrate evaluated for coating. The preferred mica is a muscovite type. Other micaceous materials such as lepidolite, biotite, phlogopite, vermiculite, and several synthetic micas were also successfully coated with various compounds. Coating glass flakes with hydrous titania from solution proved to be somewhat difficult but they were coated very nicely by thermal decomposition of organic titanates under vacuum. Several metal flakes were used as substrates but only titanium and copper withstood the coating conditions necessary for the deposition of hydrous titania. They were coated but when wet with oil ($n = 1.55$) the colors produced by the coating were considerably weakened. Coated graphite flakes exhibited the same effect when wet with an oil. Coated titanium nitride, shown by the light microscope to have a uniform TiO_2 coating, exhibited no color changes.

Just as a curiosity, several non-platey substrates such as quartz and asbestos fibers were also successfully coated with each of several metal oxides. The quartz fibers showed color changes but no color was noted with asbestos fibers. Some interest was expressed in the TiO_2-coated asbestos as a high temperature insulator. Evaluation by the Pigments Department, Newport, showed that the heat stability of the TiO_2-coated asbestos was equivalent to that of "Tipersul"* at 2,000°F. and better than "Tipersul" at 2,100°F., but poor dispersibility and weakness of the pad indicated that experimental work was necessary for the preparation of a large pad for determination of thermal conductivity. It was decided that the results were not promising enough to justify further work at this time.

*DuPont Trade Mark

Most of the coated flake products made to date utilized a Concord "200/325" water-ground muscovite mica. This mica is actually -200 mesh, containing approximately 90% -325 mesh. This type of substrate gives products much larger than the commercial nacreous pigments and therefore give a metallic effect rather than the silky effect obtained by the commercial products. Particle size of the final product, thus effect, is determined by the starting substrate. Many different fractions have been coated and evaluated. he larger particle size fraction in plastics and smaller particle size fraction in paints, inks, etc.

All coating experiment products were examined with the electron microscope to verify the coating of the substrate.

C. Coatings

Several oxides have been successfully deposited on mica but titanium dioxide, being colorless and having a high refractive index, is the oxide preferred. Such a layer of titanium oxide, in the hydrous form, is deposited upon the mica substrate by suspending the mica in a dilute strongly acidic solution of titanyl sulfate at room temperature and then hydrolyzing the titania by heating to reflux and maintaining this temperature for several hours. The hydrous oxide which is formed nucleates on the mica surface and little or no free oxide is formed. Alternatively, the mica may be suspended in hot water to which is then added a strongly acidic concentrated titanyl sulfate and hydrolysis is accomplished by heating to boil for several hours. When mica is coated with this hydrous titanium dioxide, we observe a series of colors which can be interpreted as continuous interference colors produced by varying the thickness of the oxide layer. The colors start with a silver-blue, then successively through a silver, gold, red, violet, blue, and finally a green. This color series can be repeated, giving higher order interference colors, by increasing the titania film thickness.

Electron micrographs of titania-coated mica flakes of various film thicknesses were obtained. The film is made up of fuzzy balls of unresolved titania particles which act as a continuous film. Calcination (950°C.) of the coated flakes promotes a crystal growth and now the individual titania particles are resolved and have a particle size of $\sim$ 0.06μ, but the oxide layer still functions optically as a film. With thick films (high % of hydrous titania) calcination increases the scattering of the film, thus diluting the interference color.

An example taken from the patent proposal is as follows: 580 parts of an aqueous titanyl sulfate solution containing 4.4% TiO_2 as titanyl sulfate (equiv. to 25 parts TiO_2) and F.A. of 217 is diluted with 500 parts of water. 100 parts of mica is then suspended in this solution. The mica is a water-ground white mica (muscovite) having the trade name "Concord Wet Ground Mica "200/325".

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This mica has a specific surface area of 3.3 square meters per gram, as determined by krypton adsorption in the B.E.T. method, it all passes through a 200 mesh screen and about 94% through a 325 mesh screen. The average particle size is in the range of 20-40 microns in maximum dimension and about 0.1 - 1 micron in thickness. The suspension of mica in the titanyl sulfate solution is heated rapidly (about 10 minutes) to boil and maintained at the boil under reflux for about 2-1/2 hours. The product is isolated by filtering and washing with water to a pH of 5.0. After drying at 80°C, there is obtained about 135 parts of a finely divided flake pigment which requires no further particle size reduction. In bulk form, this flake pigment is a shiny, slightly yellow powder. When dispersed in an alkyd resin vehicle and coated over a black, primed metal surface, the resulting surface has a silvery appearance and a lustrous iridescent sparkle in the sunshine.

D. Stabilization of Oxide Films

The new products containing hydrous titania on mica are very beautiful in color effects but are quite photosensitive, showing marked changes on exposure to light. Therefore, they require stabilization in this property for their most effective use. The most effective stabilization is brought about by calcination at temperatures in the range of 900-1000°C. Products calcined at lower temperatures show photosensitivity while the higher temperatures destroy the film characteristics. Products obtained by calcination retain their brilliant interference colors, although the color is shifted slightly in the direction which indicates a reduction in the film thickness (loss of sorbed H_2O and H_2SO_4). Products containing thick films show a milky character after calcination at high temperature. This milky character is attributed to the growing of large aggregates on the surface of the film, while scatter a large portion of the incident light. Partial stabilization to photosensitivity can be brought about by the deposition of certain other metal oxides on the hydrsou titania film. They will be discussed later in multi-layer systems.

E. Alternate Procedures for Film Formation

Alternative procedures for the deposition of a film of titania on mica flakes employed other water soluble salts of titanium such as titanium oxychloride and organic titanate esters. Only partial success was obtained when titanyl sulfate was replaced with titanium oxychloride. The formation of large amounts of free titania in the coating reaction gave extremely milky products. No attempt was made to improve the deposition of titania on mica from titanium oxychloride. A film of titania was deposited on hot mica flakes (±600°C.) when the vapor of an organic titanate ester such as tetraisopropyl titanate was passed over the flakes in the absence of air or water vapor and preferably in a vacuum.

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F. Other Oxide Films

Many other oxides can be deposited on mica-like substrates, some giving interference effects, others no color effect at all.

Hydrous zirconium dioxide can be deposited on mica from a solution of a suitable zirconium salt such as zirconium oxychloride or zirconium sulfate. Because the rates of hydrolysis of the zirconium salts are extremely slow, it is necessary to adjust the pH of the highly acidic solutions to increase the reaction. It is found that hydrous zirconium dioxide has a significantly lower refractive index than hydrous titania so products containing the hydrous zirconia are appreciably less nacreous than the titania products. Calcination of the coated flakes at temperatures from 700 to 1000°C. increases the refractive index, thus the nacreous character. This oxide comes closer to resembling titania than any of the other oxides studied.

Deposition of hydrous aluminum oxide on mica was accomplished in two manners: (1) thermal decomposition of aluminum acetate, and (2) slow neutralization of aluminum salt with borax in the presence of mica. The flakes are weakly nacreous and calcination at 1000°C. shows no increase in nacreous character. Micrographs show the oxide in small clusters approximately 0.2μ in diameter and after calcination the particles have a definite shape but x-ray diffraction shows no evidence of crystallinity.

Several colored oxides coated on mica give the tinctorial properties which are characteristic of the oxide, together with interference colors which range with the thickness of the oxide deposited. The oxides are conveniently deposited on the mica by bringing about a carefully controlled hydrolysis at such a rate that the mica flakes are able to function as nuclei for the oxide in question. Hydrous ferric oxide, by decomposition of ferric acetate, and chromium and vanadium oxides, from a buffered solution of these salts, are deposited on the mica substrate.

Many other oxides were deposited on mica-like substrates but gave no nacreous effect because of low refractive indices or poor film properties of the deposited oxide layer. These oxides include SiO_2, ZnO, SnO_2, Co_3O_4, NiO, MnO_2, CuO, Ag_2O ($\rightleftharpoons$ Ag), PbO, etc. Attempts to increase the refractive indices by calcination, thus increasing the nacreous character, failed with all the oxides mentioned and in most cases the film properties were destroyed. Deposition was accomplished conveniently by controlling the hydrolysis of the oxide in question in the presence of the mica substrate.

It was also discovered that layer systems of various oxides may be built up by coating one oxide upon another, etc. For example, a second layer of metal oxides may be deposited on top of titanium oxide. This second layer may consist of colorless oxides such as alumina, zirconia, zinc oxide, tin oxide, etc. On the other

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hand, it may include oxides which are colored such as iron oxide, nickel oxide, cobalt oxide, chromium oxide, etc. This second layer of oxide obviously alters the thickness of the total oxide layer and thus contributes to the interference phenomenon. Layer systems of three or four different oxides were prepared and gave results one might predict from previous work. One big advantage in depositing certain other oxides on hydrous titania is the decrease one obtains in photosensitivity. Such oxides as alumina, chromic oxide, ferric oxide give products which are not photosensitive. Some of the most unexpected results were obtained with chromium oxide. This oxide can be deposited on hydrous titania on mica by thermal hydrolysis of the chromium salt or by buffering a chromium salt solution with borax. A very thin layer ($\sim$ 1-2% Cr_2O_3) deposited on the titania layer resulted in marked stabilization without degradation of color when calcination is held at 800° C.

Further study has been undertaken to completely eliminate calcination of the pearl flake. This involves the deposition of an impervious film of hydrous silica on the titania film and will be discussed in a later report.

PROGRAM

This report terminates the work on this problem by the writer.

Further work on the process and product development of titania coated mica is being done by the Special Organics and Engineering Group, Newark, and the PTS Groups at Edge Moor and Newark.

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