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Adsorption of Pigments: The Specific Surface of Some Zinc Oxides

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This investigation was undertaken in order to determine the nature of the film adsorbed from solution on solid surfaces and to investigate the adsorption method for determining the surface area of pigments of small particle size. Zinc oxide was chosen as the pigment. Adsorption was from benzene solutions of various organic compounds.

Harkins and Gans¹ have shown that the specific surface of titanium oxide can be determined by the adsorption of oleic acid from a benzene solution, and that the amount adsorbed is constant after the concentration of the solution reaches 0.02 mole of oleic acid per 1000 g. of benzene. They have postulated that the film is monomolecular in thickness and that the film is oriented with the polar end of the molecule next to the solid surface.

Organic acids were not used in this work since it seemed likely that true chemical reaction would result between the acid and the zinc oxide. Various aliphatic chain compounds were investigated in order to find compounds which were strongly adsorbed on zinc oxide and which gave one, two and three chain molecules of a similar nature. Certain esters fit these requirements fairly well. Consequently the work reported was carried out with the three esters: methyl stearate, glycol dipalmitate and glycerol tristearate. A series of experiments was carried out also with stearyl alcohol.

(1) Harkins and Gans, *THIS JOURNAL*, **53**, 2804 (1931); *J. Phys. Chem.* **36**, 86 (1932).

Experimental Methods

The zinc oxide pigments were donated by the New Jersey Zinc Company. They will be designated as pigments 1, 2, 3, 4, and 5. They range in size from a very fine pigment, no. 1, to a coarse pigment, no. 5. The New Jersey Zinc Company's research organization has conducted extensive investigations on pigments 1, 2, 4, and 5 and has furnished the following particle size data.

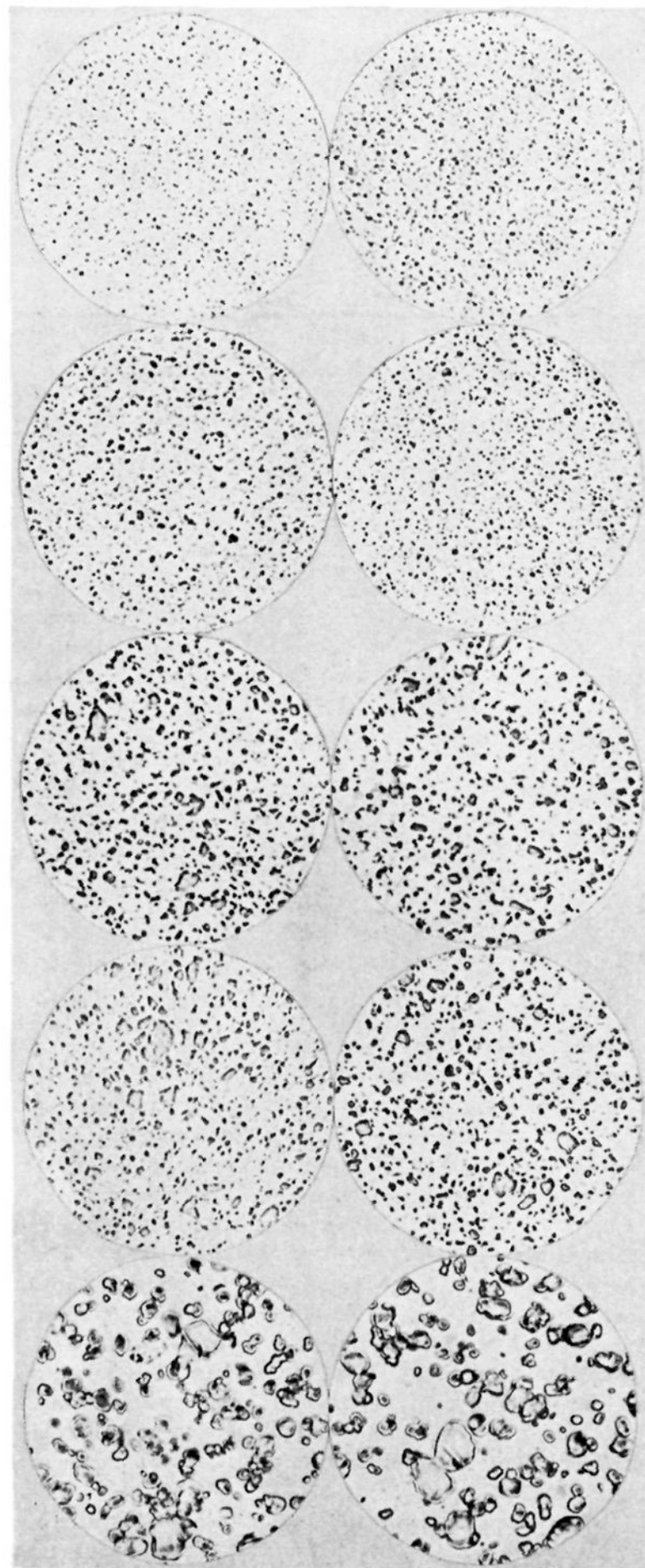
	d_1	d_2	d_3	d_4	D	S
1	0.155	0.204	0.279	0.373	0.207	3.81
2	.186	.252	.337	.421	.251	3.15
3	.370	.485	.591			1.80
4	.304	.491	.786	1.143	.490	1.35
5	.995	1.462	1.864	2.159	1.393	0.57

The diameters are given in microns. The specific surface, in square meters per gram, is calculated from the equation $S = 6/\rho d_s$, where ρ is the density of zinc oxide, 5.65 g. per cc. and $d_s = \Sigma nd^3/\Sigma nd^2$. The average diameter, $d_1 = \Sigma nd/\Sigma n$, was determined by measuring the diameters of the particles on photomicrographs. The diameter of the particle of average cross-sectional area is $d_2 = \Sigma nd^2/\Sigma nd$. d_4 is the diameter of the particle of average weight and D is the diameter of the particle of average volume.² Pigment no. 3 was a U. S. P. zinc oxide and was used as a control sample since large quantities were available. The particle size data for pigment no. 3 given in the above table were determined by the author by the photomicrographic method. Pigment no. 5 was an oxide which had been prepared by heating a superfine oxide at a high temperature until the particles had grown to a large size.

Extensive preliminary work indicated that erratic and fictitious results were obtained unless all components used in the experiments were thoroughly dry. Storage of the pigment over phosphorus pentoxide or refluxing it with the dry solvent were not severe enough treatment to con-

(2) Green, *J. Franklin Inst.*, **204**, 713 (1927).

dition the pigment. Previous work³ indicated that a zinc oxide surface could be cleaned by outgassing at a high temperature and that this treatment did not cause growth of the crystals to a measurable extent. This lack of growth



Before After

Fig. 1.—Magnification $\times 1285$.

(3) Ewing, *Ind. Eng. Chem.*, **23**, 427 (1931).

was again confirmed here by the photomicrographs of the pigments before outgassing and after outgassing, adsorption, etc. (Fig. 1). Consequently, the samples of zinc oxide were heated in Pyrex glass tubes at 480° and evacuated for twenty-four hours by means of a mercury diffusion pump. With this treatment the pressure above the hot pigment fell to less than 0.0001 mm. of mercury. This treatment probably removed adsorbed gases incident to the methods of manufacture as well as the adsorbed water. It also destroyed the zinc carbonate film which forms when zinc oxide stands in contact with the atmosphere.

The esters used were Eastman products. The benzene was a c. p. grade product. It was dried over sodium wire and was delivered to the solute, in making up the solutions, and to the pigments by means of an automatic pipet. The solutes and the solutions were stored over phosphorus pentoxide.

An adsorption experiment was conducted by sealing a weighed amount of pigment in tube A, Fig. 2. The pigment tube was then placed in the electric furnace and sealed onto the evacuating pumps. After twenty-four hours the tube was sealed off at C. Twenty-five ml. of the dried solution of known concentration was then introduced into the upper part of the tube and the seal broken at D with a stiff wire. An additional 25 ml. of benzene was then added and the tube cut off at E and tightly stoppered with a cork stopper. Tube A was then rotated, end for end, at 80 r. p. m. for twenty-four hours. Tube A was then centrifuged until the pigment was tightly packed in the bottom and the supernatant solution was perfectly clear. Twenty-five ml. of the clear solution was then pipetted into two weighing bottles for analysis and 25 ml. of benzene was added to the remaining solution in A. The pigment was then loosened up by shaking and the above procedure repeated as many times as desirable. Thus the amount adsorbed from varying concentrations of solution on a given sample of pigment was determined. Preliminary attempts to analyze the solutions of esters by hydrolysis did not give sufficiently accurate results, so a weight method was developed. Twenty-five ml. of each solution was apportioned between

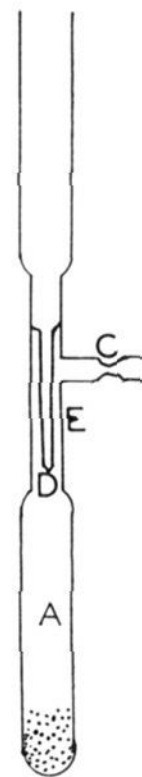


Fig. 2.

two weighing bottles, 5×1.5 cm., and weighed against a similar bottle as a tare. The bottles were then placed in an oven at 70° and a jet of air was blown onto the surface of the solutions until dry. The residues were then weighed. The weight of residue for a given solution in the two bottles seldom varied by more than 0.2 mg. per 10 g. solution. Blank runs showed that this procedure gave true results. The total amount of solute originally present and the amount in solution were determined in this manner for the first concentration. The difference is the amount adsorbed. The amount of solute removed, taking into account the solution remaining in the pipet after draining, was also determined. The difference between the total amount of solute present and the amount removed gives the total amount present in the second and the succeeding concen-

trations and thus the amount adsorbed at each concentration can be determined in the same manner as for the original concentration. At least two series of experiments were carried out on separate samples of a given pigment for each adsorbed material. Ten-gram samples of pigments 1, 2 and 3, 20 g. of 4 and 30 g. of 5 were used. Inaccuracy in the results as indicated by the deviations of the individual points from the curves are due to several causes. Two samples of a given pigment are not identical due to the varying particle sizes. This discrepancy is probably not great because of the very large number of particles in the samples taken. However, a large degree of uncertainty is introduced by the heating and outgassing procedure. This lack of reproducibility in the pigment samples causes deviations between two series of runs with the same materials. Individual deviations are probably due to experimental error in the analysis since the masses of the weighed residues varied from 2-200 mg.

The results obtained with methyl stearate and glycol dipalmitate are plotted in Fig. 3 in which the number of moles adsorbed per gram of zinc oxide is plotted against the concentrations of the solutions which are in equilibrium with the pigments containing the adsorbed layer.

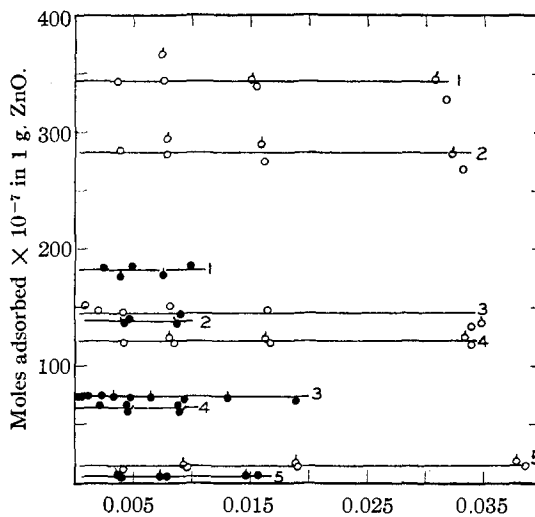
Discussion of Results

It will be noted that the average number of moles times 10^{-7} of methyl stearate adsorbed on 1 g. of pigments 1, 2, 3, 4, and 5, respectively, namely, 344, 283, 145, 122, and 15 are the same within experimental error as twice⁴ the average number of moles of glycol dipalmitate, namely, 366, 280, 148, 130, and 12. This indicates that the two compounds are adsorbed in the same manner on the solid surface and that the area occupied by the two chain molecule is approximately twice that occupied by the one chain molecule. It also strongly indicates that the film is monomolecular, or some multiple thereof, in thickness. The simple assumption to make is that it is only monomolecular in thickness. It was expected that the glycerol tristearate would occupy three times the area of the single chain. However, the data for this compound as well as for stearyl alcohol, Table I, indicate that these compounds

TABLE I
ADSORPTION ON ZINC OXIDE No. 3

Glycerol tristearate		Stearyl alcohol	
Molal concn.	Moles $\times 10^{-7}$ adsorbed	Molal concn.	Moles $\times 10^{-7}$ adsorbed
0.0071	72	0.0234	302
.0037	63	.0121	287
.0019	61	.0070	243
.0010	58	.0057	149
.0005	57	.0046	84

(4) The factor should be the actual ratio between the effective areas of the adsorbed molecules, probably $48/26.6 = 1.8$ rather than 2. 1.8 times the average number of moles of glycol dipalmitate gives, 329, 252, 133, 117 and 11.



Concentration of soln., moles solute per 1000 g. benzene.

Fig. 3.—○, Adsorption of methyl stearate, first series; ○, adsorption of methyl stearate, duplicate series; ●, adsorption of glycol dipalmitate, first series; ●, adsorption of glycol dipalmitate, duplicate series.

are much more highly adsorbed in the more concentrated solutions and that the amount adsorbed varies greatly with the concentration of the solution. It seems probable that the mechanism of the adsorption in these two cases differs from that of the first two compounds. It may well be that the selective adsorption is weak in these two cases.

Specific Surface.—If the cross-sectional area of the adsorbed molecules, and if the manner in which the molecules are adsorbed on the solid surface were known, it should be possible to calculate the surface area of the pigment. By assuming that the molecules occupy the same area as they do on a dilute hydrochloric acid surface and that the adsorbed material forms a monomolecular film completely covering the solid surface, a tentative estimate may be made of the specific surface of the pigment. Using the horizontal pull method described by Harkins and Anderson,⁵ the cross-sectional area of methyl stearate and glycol dipalmitate used in these experiments on 0.1 *N* hydrochloric acid was found to be 26.6×10^{-16} and 48×10^{-16} sq. cm., respectively. The values of the specific surfaces of the pigments calculated from these values, making use of the above assumptions, are 5.4, 4.3, 2.3, 1.9, and 0.2 square meters per gram. These areas compare favorably with those obtained by the photomicrographic measurements, 3.81, 3.15,

(5) Harkins and Anderson, *THIS JOURNAL*, **59**, 2189 (1937).

1.80, 1.35 and 0.57. The respective ratios are 10:8.0:4.3:3.5:0.37 and 10:8.3:4.7:3.5 and 1.5. The agreement in the ratios by the two methods is remarkably good except in the case of pigment number 5, the reheated oxide.

The disagreement in this case may be due to a false value by the direct measurement method since the particles are large and but few particles are present in a photomicrograph. However, several photomicrographs were used in making the measurements. More probably the disagreement is due to a sintering effect caused by the high temperature at which this pigment was manufactured and which cemented the particles together so that the complete surface was not free to adsorb the solutes. The rubbing down process in making the photomicrographs breaks down these sintered aggregates. It is also possible that it breaks up some of the actual particles and, further, that in applying pressure in preparing the microscopic slides some of the largest particles are crowded out of the field of vision. Which surface in these aggregated samples is of more practical value depends on the processing to which the pigment is subjected in use. If, for example, the pigment is completely dispersed in a paint or rubber compound, the photomicrographic surface should offer a truer picture of facts. If the aggregates are not dispersed, the adsorption surface should be better.

There is uncertainty as to the correctness of the actual values of the specific surfaces due to inherent faults in either method. In the photomicrographic method this is due to the assumption that the particles are spherical and to the necessary assumption as to the size of the colloidal material present since the microscope does not resolve the colloidal particles.⁶ In the adsorption method this is due to the heat treatment necessary to clean the surface. This heat treatment undoubtedly causes some growth resulting in the disappearance of some of the colloidal particles. There is also a probability that the surface occupied by a molecule on a liquid surface is not the same as on a crystalline surface.

An effort was made to check the adsorption results by analyzing the residues after the experiments were completed. The results were of the same magnitude as obtained above but due to experimental difficulties no reliance could be placed on the actual values obtained.

(6) Gamble and Barnett, *Ind. Eng. Chem., Anal. Ed.*, **9**, 310 (1937).

It is difficult to assign these adsorptions to any of the well-known mechanisms. If the adsorption is due to a chemical reaction between the pigment and the adsorbed material, the amount of adsorption should increase with time unless an impervious layer is formed. Chemical action was tested for by preparing a sample in the usual manner using methyl stearate and removing 5-ml. samples after seven hours and thereafter at twenty-four hour intervals for eight days. All these samples gave the same concentration on analysis, showing that chemical reaction was not proceeding after the adsorption had reached the usual equilibrium.

The curves in Fig. 3 show that the Freundlich type of adsorption is not followed unless it should be in the extremely dilute region not covered by these experiments, and unless the experimental procedure here used is not drastic enough to establish equilibrium between adsorbed and dissolved reagent on diluting the solution. Even in the cases of the stearyl alcohol and the glycerol tristearate, where adsorption changes with concentration, the Freundlich type of curve is not obtained.

There is also the possibility that the adsorbed molecules do not have the same spatial arrangement on a crystal surface that they have on a liquid surface. It might be, for example, that each adsorbed molecule, or each polar group in each adsorbed molecule, is held by the free valence forces of the zinc unit or the oxygen unit in the surface of the crystal. If this were true the area of the adsorbed molecule used in calculating the specific surface would not be its area on a hydrochloric acid surface, but would be the area occupied by the zinc or oxygen unit in the surface of the zinc oxide crystal. In order to investigate this possibility it is necessary to examine the area of the units in the faces of the crystal relative to the cross-sectional area of the adsorbed molecule. Zinc oxide crystallizes in the hexagonal close-packed system. Natural crystals usually have the habit of hexagonal prisms, the developed prism faces being either first order (10·0) or second order (11·0). Along the first order prism face the area associated with each zinc unit (or each oxygen unit) is 16.9 \AA^2 and along the second order prism face, 14.6 \AA^2 .⁷ In the ends of the prism on faces perpendicular to the principal axis (basal plane (00·1)) the area associated with each zinc

(7) Fuller, *Science*, **70**, 196 (1929).

