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The Activation of Titanium Dioxide as a Decontaminant for Radioactive Contamination

By Toshiko TAKAMI and Tsunetaka SASAKI

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo

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The decontamination efficiencies of treated and untreated titanium dioxide pastes were measured using ^{60}Co-contaminated surface of plastics, polyvinyl chloride. The titanium dioxides used were commercial titanium dioxide, hydrous titanium dioxide, titanium dioxide treated with sulfuric acid, and "Titanium Cake," an intermediate product of the titanium dioxide industry. Among these titanium dioxide decontaminants, titanium dioxide treated with sulfuric acid proved most effective in decontamination, even in neutral conditions, if activated properly. The optimum condition of activation was the 50% sulfuric acid treatment of commercial titanium dioxide at 50°C for 6 hr.

For the radioactive decontamination of a solid surface, we generally use radioactive decontaminants. These decomtaminants vary according to their purposes. In this connection, it is important to note that the residual contamination remaining even after a rough decontamination is often a matter of intense interest. Such a decontamination is often influenced by the nature and not by the amount of the decontaminant used. As for the decontaminants, such powdered substances as titanium dioxide,[1] alumina[1] and kaolin[2] are used. These substances are usually applied as pastes. Among these, titanium dioxide is comparatively effective and is widely used. However, little is known concerning its decontaminating action except for the facts that anatase is superior to rutile and the fresh precipitate is even more excellent.[1,3,4] However, it is troublesome to prepare a fresh precipitate from commercial titanium dioxide or a soluble titanium compound prior to each decontamination. It is, however, a usual practice in the preparation of an adsorbent to promote the adsorption capacity by the suitable treatment of its surface. Therefore, we desired to find a simple and effective method of activating a commercial titanium dioxide without complete dissolution, for the use as a decontaminant.

In the present investigation, the activation of titanium dioxide by sulfuric acid was undertaken for this purpose.

Experimental

Sample.—From the results of a preliminary experiment contaminating the solid surface of polyethylene, polystyrene and polyvinyl chloride, polyvinyl chloride was chosen as the test surface since it was comparatively more susceptible to contamination than the other specimens. A commercial product of polyvinyl chloride, 0.75 cm. thick and cut in a 2.5×2.5 cm. size, was used as the test piece. An aqueous solution of cobaltous chloride labeled with radioactive ^{60}Co was used as the contaminating solution, the concentration being 5.20×10^{-3} mol./l., and the specific activity, 19 c./mol. The titanium dioxide used as a decontaminant was a commercial product of the anatase type.

Experimental Procedure.—For the preparation of the contaminated sample, a test piece was soaked in a 0.5% solution of Epan 485 (a block copolymer composed of polyoxyethylene and polyoxypropylene, a Daiichi Kogyo Seiyaku product) to remove any oily contamination from the surface, rinsed with distilled water, and dried using filter paper. To contaminate the test piece, filter paper 2.0×2.0 cm. in size which had been soaked with 5 ml. of a radiaoactive ^{60}CoCl$_2$ solution over a 24 hr. period, was placed on the sample for contamination. After an hour the filter paper was removed and the sample was immersed in water to rinse off the easily removable excess contaminant, the radioactivity was then measured using a Geiger-Müller counter (Aloka GP-1; window thickness: 1.4 mg./cm^2), with the sample placed 1 cm. below the counter tube. The amount of cobalt on the sample was calculated from this counting rate and the counting rate of a known amount of the cobaltous chloride, which was put in small droplets on a polyvinyl chloride sample and dried. Figure 1 shows the contamination remaining after such a treatment plotted against the time of washing. Here, the percentage of cobalt remaining on the surface was calculated from the counting rates observed for the test piece before and after the contamination. From this curve, it is difficult to distinguish between the contamination merely adhering to and that adsorbing on the solid surface. However, the initial, rapidly decreasing portion of the curve was

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[1] H. A. Künkel, *Strahlenther.*, **90**, 100 (1953); **91**, 326 (1954).

[2] Ya. Nosek and V. Khemelorzh, *Med. Radiol.*, **4**, 74 (1954).

[3] H. Hotta and H. Nakamura, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **81**, 1 (1960).

[4] National Bureau of Standards Handbook U. S. A., 48 (1951).

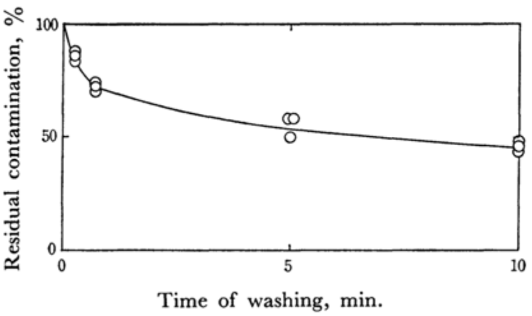

Fig. 1. Residual contamination vs. time of washing by water.

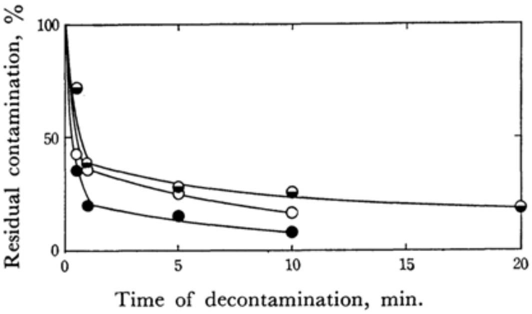

Fig. 2. Residual contamination vs. time of decontamination.
○ Commercial titanium dioxide
● Hydrous titanium dioxide
◒ Distilled water alone

conveniently taken as due to the adhering contamination, and 1.5 minutes' washing was adopted for the preparation of a standard sample of the contamination. For further decontamination measurements, a 2 g. portion of titanium dioxide was mixed with 0.7 ml. of distilled water to make a paste, with which the sample was then put in close contact. After 5 min., the surface was rinsed with water for 30 sec. to remove the decontaminant, dried using filter paper, and the surface counting rate was measured. In these experiments, the pH of the paste was adjusted to 5.0—5.5 to avoid the co-operating action of hydrogen ions mentioned later. Also the mechanical action was not applied in order to study exclusively the chemical decontaminating action of the powder itself. In comparison with this, the decontamination experiment using distilled water without the powder was made in a shallow dish 2.4×2.4×0.3 cm. in size. The sample was then similarly risned, and the amount of contamination was measured. Figure 2 shows the residual contaminations obtained with commercial titanium dioxide, hydrous titanium dioxide and distilled water without titanium dioxide, where the contaminations were plotted against the decontamination time. It may be seen in Fig. 2 that the residual contamination decreases rapidly in the initial one or two minutes, followed by a slow decrease in every case. Therefore, in the following experiments, the time of decontamination was properly chosen as 5 min., as has been mentioned above, after which the decrease in contamination was seen to be fairly slow. In discussing the effect of decontamination, the percentage of residual contamination,

$$\frac{\text{Residual contamination after 5 min.}}{\text{Initial contamination on standard sample}} \times 100$$

was used. All experiments were carrid out at room temperature (about 20°C).

Results

Decontamination by Commercial Titanium Dioxide and Hydrous Titanium Dioxide.— It is generally believed that freshly-precipitated titanium dioxide shows a strong decontamination power. Therefore, the hydrous titanium dioxide was prepared as follows.[5] About 24 g. of a commercial titanium dioxide was slowly dissolved in 60 ml. of concentrated sulfuric acid, stirred, and evaporated to dryness by heating it at 230°C for an hour. The product was then dissolved in 100 ml. of distilled water and filtered to remove any insoluble matter. The filtrate was neutralized with sodium hydroxide, and the precipitates formed were separated by decantation. It was then dried at 100°C for 24 hr., ground in a mortar, suspended in water, and heated to 70°C. The suspension was neutralized with hydrochloric acid, washed by repeated decantation using water, and dried. Thus, about 16 g. of neutral hydrous titanium dioxide was obtained.

Table I. Decontamination efficiency near neutral pH

Decontaminant	Initial contamination mol./4 cm^2 $\times 10^{10}$	Residual contamination mol./4 cm^2 $\times 10^{11}$	Residual contamination %
Water alone	1.11	3.31	29.8
Commercial titanium dioxide	1.92	3.95	20.5
Hydrous titanium dioxide	2.36	4.14	16.8
Titanium Cake A	1.88	4.76	25.3
Titanium Cake B	2.74	7.44	27.1

Table I shows the decontamination efficiency obtained for hydrous titanium dioxide, commercial titanium dioxide and water without titanium dioxide. It may be seen in this table that the addition of titanium dioxide to water evidently increases the decontamination efficiency and that the hydrous titanium dioxide shows a greater decontamination efficiency than the untreated one. The hydrous titanium dioxide reduced the remaining contamination to 50% of that obtained for the sample treated with distilled water alone. Therefore, hydrous titanium dioxide may be a better

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5) W. B. Blumenthal, *Ceram. Age,* **51**, 320 (1948).

decontaminant than the untreated commercial product, which exhibits an 80% residual contamination, but it cannot be considered so effective a method of preparing a decontaminant, considering the concentrated sulfuric acid, the fairly high temperature and the exhaustive decantation required for the preparation of hydrous titanium dioxide.

Decontamination by Titanium Dioxide Treated with Sulfuric Acid.—We further attempted to prepare a more effective decontaminant by a more simple treatment of the commercial titanium dioxide powder, that is, by a mere surface treatment of titanium dioxide by sulfuric acid, without the total dissolution of the titanium dioxide.

Activation with Concentrated Sulfuric Acid.—About 20 g. of commercial titanium dioxide was treated with 20 ml. of concentrated sulfuric acid at 8, 20, 30, 50, 100 and 200°C for an hour, washed with water until it became neutral, and filtered. Table II shows the decontamination efficiencies for these samples. It may be seen in this table that the decontamination efficiency increased with the temperature of treatment, and that the maximum decontamination efficiency was attained above 50°C, regardless of the temperature. It was further confirmed that acid-treated titanium dioxide was more effective than hydrous titanium dioxide and, of course, than untreated titanium dioxide. In the above treatment, however, it was still troublesome to wash the treated sample with water alone, until it became neutral, although the time required for washing was remarkably shortened as compared with the case of the preparation of hydrous titanium dioxide mentioned above. Therefore, we further attempted to compare the difference in the decontamination efficiency of acid-activated (30°C, 1 hr.) titanium dioxide samples treated by the following three different methods of washing: washing until neutral with water alone; the addition of sodium hydroxide until the pH value of 2 was reached, followed by washing with water until neutral, and direct neutralization with sodium hydroxide. The results are shown in Table III.

TABLE II. EFFECT OF TEMPERATURE ON SULFURIC ACID TREATMENT OF TITANIUM DIOXIDE

Temp. °C	Initial contamination mol./4 cm^2 $\times 10^{10}$	Residual contamination mol./4 cm^2 $\times 10^{11}$	Residual contamination %
8	6.74	9.99	17.4
20	2.21	2.58	11.7
30	2.78	3.30	11.0
50	1.44	1.30	9.0
100	8.07	7.38	9.1
200	7.25	7.21	9.8

TABLE III. EFFECT OF NEUTRALIZATION METHOD ON ACTIVATED TITANIUM DIOXIDE

Method	Initial contamination mol./4 cm^2 $\times 10^{10}$	Residual contamination mol./4 cm^2 $\times 10^{11}$	Residual contamination %
Washing with water until neutral	2.78	3.30	11.0
Addition of NaOH until neutral	1.62	1.65	10.2
Addition of NaOH to pH 2 and washing with water	6.19	7.11	11.0

In this table, little difference in decontamination efficiency is seen amoung the treatments. From this, it may be concluded that direct neutralization by sodium hydroxide can be adopted to reduce remarkably the time of washing compared with mere washing with water. Therefore, the direct neutralization method was adopted in the following experiments.

Activation with Diluted Sulfuric Acid.—Attempt was then made to activate titanium dioxide with diluted sulfuric acid, since it is easier and desirable to use a diluted sulfuric acid than the concentrated one. The effects of the temperature and the time

TABLE IV. DECONTAMINATION EFFICIENCY OF ACTIVATED TITANIUM DIOXIDE UNDER VARIOUS CONDITIONS

Concn. of H_2SO_4 wt. %	Temp. °C	Time hr.	Initial contamination mol./4 cm^2 $\times 10^{10}$	Residual contamination mol./4 cm^2 $\times 10^{11}$	Residual contamination %
15	50	6	2.45	2.88	13.0
15	50	24	1.52	1.90	12.5
30	50	6	2.44	3.12	13.1
30	50	24	2.76	3.92	10.7
40	50	6	3.48	3.77	10.9
40	50	24	3.26	3.26	10.0
50	50	6	1.15	1.07	9.3
50	30	1	2.86	5.25	18.4
50	30	3	1.61	1.97	12.2
50	30	6	1.60	1.91	11.9
50	30	24	0.937	1.04	11.1
75	30	1	5.60	6.99	13.9

of treatment on the decontamination efficiency under such conditions were examined. The results are shown in Table IV. From this table it may be seen that the temperature of treatment has a greater effect than the time of treatment above a 50% sulfuric acid activation. In the case of 30% sulfuric acid activation, the time of treatment is four times as long as that of the 50% sulfuric acid treatment needed to achieve the same decontamination efficiency. In the case of 15% acid activation, an even longer time is required.

Decontamination with "Titanium Cake."—The above experiments suggest that the so-called "Titanium Cake," that is, the wet intermediate product of the titanium dioxide industry, would be equally excellent as the acid-activated titanium dioxide in decontamination efficiency. Therefore, the decontamination efficiency was similarly examined with "Titanium Cake" with a pH value of about unity. The results are shown in Table I, where the pH of this paste was controlled with sodium hydroxide to 5.0—5.5. Contrary to the above expectations, "Titanium Cake" in a neutral-pH paste was little different in decontamination efficiency from distilled water alone, in spite of the wet nature of the "Titanium Cake."

Decontamination in an Acid Region.—It is further known that the decontamination efficiency of a decontaminant generally increases in an acid region, in addition to the action of the acid itself.1) Therefore, the decontamination efficiencies of various titanium dioxide pastes were compared at a pH value of unity. The results are shown in Table V. Here, the pH values of "water alone" and commercial titanium dioxide were controlled with hydrochloric acid to unity, while acid-activated titanium dioxide was prepared under the optimum conditions of 50% sulfuric acid treatment at 50°C for 6 hr., followed by the addition of sodium hydroxide until a pH value of unity was reached, and the "Titanium Cake" with a pH value of unity was used without further control of the pH. These results confirm the view that the action of acid itself is remarkable in the decontamination, as can be seen from a comparison of the results of Tables IV and V. However, we can see a still further increase in the decontamination efficiency upon the addition of titanium dioxide; here again, acid-treated titanium dioxide proves to be best, as is to be expected.

TABLE V. DECONTAMINATION EFFICIENCY IN ACID REGION

Decontaminant	Initial contamination mol./4 cm^2 $\times 10^{10}$	Residual contamination mol./4 cm^2 $\times 10^{11}$	Residual contamination %
Water alone	2.07	2.77	13.4
Commercial titanium dioxide	3.79	3.28	8.7
Activated titanium dioxide	9.14	2.90	3.2
Titanium Cake A	7.29	2.89	4.0
Titanium Cake B	8.80	5.00	5.7

Conclusion

It may be concluded from the results of the above investigation that an effective decontaminant for a surface of plastics contaminated with ^{60}Co is prepared by the surface treatment of titanium dioxide with sulfuric acid. The optimum conditions are treatment with 50% sulfuric acid at 50°C for 6 hr., but if we allow somewhat of a lowering of the decontamination efficiency, a 30% sulfuric acid treatment at 50°C for 24 hr. can also be recommended. These are more practicable conditions. The lowering of the temperature below 50°C resulted in a decrease in effect unrecoverable even by treatment over a prolonged time, this is in contrast to the decrease in efficiency produced by the lowering of the concentration of sulfuric acid which is recovered by a prolonged treatment. As for the pH dependence, it has been confirmed that the decontamination efficiency rises more remarkably in the acid region (pH unity) than near the neutral pH. "Titanium Cake," obtainable as a wet paste, is expected to be favorable for use as a decontaminant. The results of the measurements, however, show that in the neutral region, it is no more better than water without titanium dioxide, although it is nearly equal in its effect to acid-treated titanium dioxide in the acid region.

As for the titanium dioxide decontaminant, it is usually applied on a solid surface as a paste in 0.1 N hydrochloric acid. In this case the hydrogen ion and mechanical action during performance assist the decontaminating action, in addition to the chemical action of titanium dioxide itself. However, it is not always allowable to lower the pH of the decontaminating solution and, further, to rub the surface effectively, because of the susceptibility to damage and the complicated shape of the solid surface. Also, the solid surface may often be scratched by rubbing, and thus, rendered to be liable to subsequent strong contamination. Consequencly, the titanium dioxide, even without such acid and mechanical actions, should have a good decontamination power in order to be effective under widely differing conditions of decontamination. In the present experiment, therefore, the mechanical effect of rubbing was avoided. The rubbing, if applied, would promote and make the decontamination efficiencies of almost all of the samples indistinguishable, but the subsequent contamination would become more marked. It may be inferred, further, that the acid-treated titanium dioxide may be more highly recommended as a decontaminant than ordinary titanium dioxide, where a trace of residual radioactive contamination causes a serious problem, as in the case of skin contamination.

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