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## METHOD AND COATING COMPOSITION FOR PROTECTING AND DECONTAMINATING SURFACES

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This invention relates to protective coatings, and more particularly to a coating composition which is advantageously utilized as a protective coating for surfaces which are exposed to radioactivity.

Generally speaking, in the neutron irradiation of uranium, uranium metal in the form of slugs is subjected to neutron irradiation for the desired period of time, and withdrawn from the irradiation zone and allowed to undergo a suitable aging period, advantageously a period of about 60 days in order to reduce the radioactivity of the slugs and to allow the bulk of the neptunium present to decay to plutonium. Following this aging period, the slugs are dissolved to form a highly radioactive solution, which solution may be subjected to a suitable chemical treatment in order to isolate therefrom plutonium, or if desired, to separate individual fission products or groups of fission products. In these separation processes, it is necessary to shield the operators because of the highly radioactive nature of the solutions.

In addition to the large scale methods of separating the constituents of neutron irradiated uranium, the operation of laboratories devoted to a study of the properties of highly radioactive material generally requires the enclosure of laboratory apparatus within concrete or similar protective shielding.

When the walls or floors of the cells enclosing apparatus for processing radioactive material have heretofore become contaminated, great difficulty has been experienced in removing this contamination from the wall or floor surface. For instance, there have been cases where spillage of radioactive liquid has occurred upon concrete which was immediately washed with an aqueous nitric acid wash. This acid wash failed to decontaminate the concrete surface satisfactorily. In order to decontaminate the concrete surface to such an extent that personnel could safely work in proximity thereto for a considerable period of time, it was necessary to grind off the concrete to a depth of about  $\frac{1}{32}$  of an inch.

Such a procedure of obtaining decontamination of concrete surfaces is undesirable, among other reasons, in that it requires exposure of personnel to the contaminated surface during the decontamination operation. Furthermore, a problem of disposal of solid material removed from the surface is presented.

We have found that surfaces which may be exposed to spillage of radioactive liquids, or which otherwise may become contaminated with radioactivity, may be put into a condition susceptible of ready decontamination by previously applying thereto certain readily removable coatings.

It is accordingly an object of this invention to provide a process for protecting surfaces which may be exposed to radioactive contamination.

It is another object of this invention to provide a readily removable coating which is capable of protecting surfaces from radioactive contamination.

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Still another object of this invention is the provision of a water soluble coating composition capable of protecting a surface from radioactive contamination, and of such a nature as to be readily deposited upon and separated from the surface to be protected.

A further object of this invention is the provision of a protective coating composition which is sufficiently water soluble to be removable by water spray and yet sufficiently water insoluble to withstand removal by the spillage of aqueous radioactive solutions thereon.

It is still another object of this invention to provide a readily removable protective coating capable of withstanding aqueous radioactive solutions and comprising a water soluble carbohydrate and a hygroscopic agent.

A further object of this invention is to provide a process of preparing a readily removable protective coating for various surfaces which is capable of resisting the action of radioactive material.

These and other objects of our invention will become apparent to the skilled worker in the art upon becoming familiar with the following description.

In accordance with our invention, the most advantageous coating compositions are water soluble compositions which may be sprayed or brushed onto the surface to be protected. While the compositions are indicated as water soluble, they must not be too water soluble or otherwise the spillage of aqueous radioactive solution thereon would remove the protective coating. On the other hand, they should be sufficiently water soluble to be removable by water spray, as it is not possible, because of radiation hazard, to get in close proximity with the coating for scouring it off.

We have found that particularly advantageous water soluble coating compositions may be prepared by carefully admixing a water soluble carbohydrate with water and thereafter adding a hygroscopic agent.

Examples of water soluble carbohydrates which may be employed in preparing the protective coating compositions of our invention are glycoaldehyde, erythrose, ribose, mannoheptose, levulose, sucrose and starch dextrins such as tapioca starch dextrin, potato starch dextrin, rice starch dextrin, wheat starch dextrin and the like. Advantageous results may be obtained in the practice of our invention by utilizing starch dextrins as exemplified above. Particularly advantageous results may be obtained in the practice of our invention by employing in the composition a tapioca starch dextrin known as "Tapoganth."

Examples of hygroscopic agents which may be employed in the practice of our invention are calcium bromide, calcium chloride, zinc chloride, zinc bromide, and the like. Particularly advantageous results are obtained by utilizing calcium chloride as a hygroscopic agent in our composition.

While the proportions of ingredients in our water soluble coating compositions may be varied, depending, among other things, upon the surface to be protected, the atmosphere in which the surface is located, and the like, generally speaking, advantageous results may be obtained by utilizing a composition containing 15 to 25% by weight of water soluble carbohydrate, 70 to 80% by weight of water and 5 to 15% of a hygroscopic agent.

In some instances, when the coating composition is to be exposed to atmospheres of comparatively low humidity, it may be desirable to incorporate into the composition a small amount, such as up to 5% by weight of a plasticizing agent. Examples of suitable plasticizing agents are polyhydric alcohols such as glycerine, ethylene glycol, and the like, and ethers of polyhydric alcohols such as 2-ethoxyethanol and the like. Plasticizing agents such as glycerine and ethylene glycol may also serve as



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hygroscopic agents under certain conditions. However, generally speaking, in the practice of our invention the beneficial results obtained by the use of such hygroscopic plasticizing agents are apparently due to a plasticizing action which is not a result of the hygroscopic qualities thereof. However, our invention is not intended to be limited by any theory advanced herein.

The ratio of water to water soluble carbohydrates in our compositions may vary somewhat depending upon the manner in which they are to be applied to the surface to be protected. For example, a composition suitable for brushing may contain approximately  $3\frac{1}{2}$  parts by weight of water to 1 part by weight of tapioca starch dextrin. Whereas, a composition suitable for spray application may contain 4 parts water per part of tapioca starch dextrin by weight.

The compositions may be prepared by adding the required amount of water to a suitable container and, while vigorously agitating the water, adding the required amount of water soluble carbohydrate. The mixture may then be agitated until all of the water soluble carbohydrate is uniformly dispersed, which agitation generally requires about a half-hour. After admixing the above ingredients as indicated, the required amount of hygroscopic agent is slowly added to the solution while continuing the vigorous agitation, preferably avoiding lumping of the hygroscopic agent or an appreciable rise of temperature of the mixture. The hygroscopic agent is advantageously incorporated into the mixture in the form of a powder. It is generally desirable, after the admixing of the above-mentioned ingredients, to incorporate a suitable dye such as fluorescein, and the like. The dye serves to indicate that the paint has been applied to a surface and to facilitate estimates of relative film thickness and uniformity.

Our invention may be more readily understood by reference to the following specific examples which are given merely by way of illustration and are not to be considered in a limiting sense.

## EXAMPLE I

A 1-gallon batch of paint was prepared utilizing a ratio of 4 parts of water to 1 part tapioca starch dextrin by weight. The water was added to a large glass beaker and a mechanical agitator therein was started. The required amount of tapioca starch dextrin was then added over a period of several minutes. This mixture was agitated until all of the tapioca starch dextrin was uniformly dispersed, which required about one-half hour. This gave a brown mixture having a pH of about 8.6. Powdered  $\text{CaCl}_2$  in an amount equal to about 10% of the total solution weight was then added slowly while continuing the agitation, avoiding building up lumps of  $\text{CaCl}_2$  in the paint or appreciable temperature rise. After  $\text{CaCl}_2$  addition, the pH was about 7.2. Approximately 1 g. of fluorescein was added to the approximately 1-gallon batch to give a yellow color. The stirrer was then removed and the paint allowed to stand for an hour or two in order to permit the air bubbles and foam to disappear.

The paint described in Example I, upon standing, developed a gelatinous precipitate which settled out from the composition. However, this precipitate had no effect on the application of the paint.

In a modification of our invention, the tapioca starch dextrin-water solution may be allowed to stand overnight before the addition of calcium chloride. This decreases the amount of precipitate which settles out from the paint while standing. Another and particularly advantageous method of decreasing this precipitate is by adjusting the pH of the paint batch to approximately 6.8 by addition of hydrochloric acid.

The application of a paint such as that prepared in accordance with Example I may be facilitated by incorporating therein approximately  $\frac{1}{2}$  to 1% of an emul-

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sifying agent such as sodium oleate, aromatic sulphonates, sodium lauryl sulfate and the like.

## EXAMPLE II

A water soluble paint having the following composition was prepared in the following manner:

Ingredients per gallon:

6 pounds  $\text{H}_2\text{O}$   
0.02 pound wetting agent  
1.5 pounds tapioca starch dextrin  
0.75 pound powdered  $\text{CaCl}_2$   
0.05 pound 20%  $\text{HCl}$   
0.002 pound fluorescein  
0.4 pound glycerine

A two-gallon batch of the above composition was prepared by adding 5440 cc. (12 lbs.) of water to a large container and starting the agitator immersed therein. Approximately 18 grams (0.04 pound) of wetting agent in the form of an 85% paste of the dioctyl ester of sodium sulfosuccinic acid were then added and allowed to dissolve nearly completely, which took about 15 minutes. Thereafter, 3 lbs. of tapioca starch dextrin was slowly added over a period of about 15 minutes and the mixture was agitated until homogeneous, which took about 30 minutes. Subsequently 0.75 pound of powdered  $\text{CaCl}_2$  was added slowly over a period of about 15 minutes. Thereafter 40 cc. of a solution of 37%  $\text{HCl}$  diluted with an equal volume of water were added and the agitator stopped and the mixture allowed to set for two hours. The agitator was then started and 0.75 lb. of powdered  $\text{CaCl}_2$  was slowly added to the mixture over a period of about 15 minutes. Then 40 cc. of the 37%  $\text{HCl}$  solution diluted with an equal volume of water were poured slowly into the composition. Thereafter 2 grams of fluorescein were added and finally 290 cc. (0.8 lb.) of glycerine were added. The mixing was continued for 10 minutes, then the agitator was stopped and the composition allowed to set for one hour to permit bubbles to rise.

## EXAMPLE III

Another batch of paint containing the same ingredients as those set forth in Example II, with the exception that the glycerine was omitted, was prepared in a manner similar to that set forth in Example II.

The coating compositions of our invention may be applied by any suitable means, such as by pouring, spraying, or brushing upon the surface to be protected from radioactive material. In the event that spillage of radioactive solutions or condensation of radioactive vapors occurs upon the coated surface, the coating and radioactive material thereupon may be conveniently washed from the surface by means of a spray of water from a considerable distance, thereby eliminating the necessity of operators coming in close proximity to the radiation of the radioactive solution. For instance, removal may be accomplished by means of spray heads appropriately placed within a cell and remotely controlled from a point outside of the cell. The compositions of our invention are particularly suitable for application to concrete shielding such as is commonly employed to protect operators from hazardous radiation when handling radioactive solutions. However, the compositions may also be applied to other types of shielding such as metal, for example 25-12 stainless steel.

The compositions of our invention were subjected to tests in the following manner: 4' x 4' test panels made of  $\frac{1}{4}$ " Masonite were painted with 3 brush coats of a gray acid resistant paint of a type generally employed in painting concrete shielding. At least 24 hours drying time was allowed between coats. A paint similar to that prepared in Example I was sprayed on these panels with a standard Binks paint spray-gun with the spray moved fairly rapidly over the surface, and with few enough passes during the



application of each coat to avoid running. Approximately 10 minutes drying between coats allowed sufficient drying to prevent running of the next coat. From 4 to 6 coats were applied in each case, and the resulting films appeared dry to the touch within two or three hours. The films, after standing overnight in an open roofed over area, were washed off the panels with cold tap water applied through a shower-bath head on the end of a hose. The water flow was adjusted to about 5 gallons per

contaminating solutions were dried at room temperature for 24 hours or under a reflector drying lamp or in an oven at 40° to 60° C. for 2 hours. The data from these 1" x 1" panel decontamination tests are shown in Table A, and the decontamination factors

(Original activity noted)  
(Final activity noted)

are summarized in Table B.

Table A.—Decontamination of one inch by one inch panels by washing off water-soluble film (concrete and Transite panels painted with oil paint, 25-12 stainless ones not)

A. CONTAMINATED WITH Na<sub>2</sub>CO<sub>3</sub>—NEUTRALIZED PLANT NON-METAL WASTE

| No.    | Film  | Panel         | Beta Counts/Minute <sup>a</sup> |                            |                 | Gamma Counts/Minute <sup>a</sup> |                            |                 |
|--------|---|---------------|---------------------------------|----------------------------|-----------------|----------------------------------|----------------------------|-----------------|
|        |   |               | Contam-<br>inated               | After 30<br>Minute<br>Wash | DF <sup>b</sup> | Contam-<br>inated                | After 30<br>Minute<br>Wash | DF <sup>b</sup> |
| 1..... | None.....   | 25-12.....    | 3,263                           | 373                        | 8.7             | 149                              | 20                         | 7.5             |
|        |   |               | 2,830                           | 348                        | 8.1             | 135                              | 18                         | 7.5             |
|        |   | Concrete..... | 1,492                           | 422                        | 3.5             | 72                               | 16                         | 4.5             |
|        |   |               | 2,066                           | 732                        | 2.7             | 84                               | 19                         | 4.4             |
|        |   |               | 828                             | 352                        | 2.3             | 58                               | 36                         | 1.6             |
| 2..... | Tapioca starch<br>dextrin—CaCl <sub>2</sub> ..... | 25-12.....    | 1,040                           | 26                         | 40              | 48                               | 0                          | ∞               |
|        |   |               | 1,140                           | 14                         | 81              | 52                               | 4                          | 13              |
|        |   | Concrete..... | 1,270                           | 61                         | 21              | 69                               | 1                          | 69              |
|        |   |               | 848                             | 41                         | 21              | 41                               | —4                         | ∞               |
|        |   |               | 1,612                           | 52                         | 31              | 114                              | 24                         | 4.8             |

<sup>a</sup> Beta counts, cellophane sheet absorber; gamma counts, 446 mg. Al/cm.<sup>2</sup> absorber. All counts corrected for background (ca. 24 counts/minute for gamma).  
<sup>b</sup> DF=decontamination factor.

Table B.—Summary of water-soluble film tests on one inch by one inch panels

| Film  | Beta Decontamination Factors |                       |                 |                       | Gamma Decontamination Factors |                       |                |                       |
|---|------------------------------|-----------------------|-----------------|-----------------------|-------------------------------|-----------------------|----------------|-----------------------|
|   | Alkaline Waste               |                       | Acid Waste      |                       | Alkaline Waste                |                       | Acid Waste     |                       |
|   | 25-12                        | Concrete <sup>a</sup> | 25-12           | Transite <sup>a</sup> | 25-12                         | Concrete <sup>a</sup> | 25-12          | Transite <sup>a</sup> |
| None.....   | 8                            | 3                     | -----           | 9                     | 8                             | 4                     | -----          | 19                    |
| Tapioca starch<br>dextrin—CaCl <sub>2</sub> ..... | 61                           | 24                    | <sup>b</sup> 98 | 303                   | 25                            | 11                    | <sup>b</sup> ∞ | 150                   |

<sup>a</sup> Concrete and Transite panels painted with oil paint, 25-12 stainless ones not.  
<sup>b</sup> Beta decontamination factor reduced to 20 (gamma to 17) when active solution allowed to soak on film for six hours to three days, without drying.

minute which gave low impinging force and the spray was distributed evenly over the panel by manually moving the shower head. To minimize water consumption, the spray was applied to the panel only 1/5 of the time; at first, 1/2 minute spray, then 2 minutes off, and later 1 minute spray and 4 minutes off, repeating this for a total of 31 minutes. With this method of washing, all of the film was removed completely in every case with a total water consumption of two gallons per square foot. The above described test indicates that the films formed by the application of the paints of our invention are readily removable from a surface by water spray.

Tapioca starch dextrin-calcium chloride mixtures were then tested for decontamination by contaminating 1" x 1" panels of 25-12 stainless steel, painted concrete, and painted asbestos board with waste solution from a plant for the chemical separation of the components of neutron irradiated uranium, with and without previous protection by water soluble films prepared as indicated in the above examples. The initial beta and gamma activities of the panels were measured after drying. After washing the panels for 30 minutes in cold running water and again drying, the remaining activity was measured. The radioactive solutions were applied to the horizontal panels from pipettes using about 0.5 to 1.0 cc. per 1" x 1" panel, the solution forming a puddle which was allowed to dry before the activity of the panel was measured. The

In the above tables, the beta decontamination factors are the more reliable, due to the approximately 10 fold higher counting level. Decontamination factors were somewhat larger on 25-12 stainless steel than on painted concrete or asbestos board panels, and were larger with the more active plant metal waste than with the neutralized non-metal waste. These results show the tapioca starch dextrin-CaCl<sub>2</sub> film capable of obtaining decontamination factors greater than 100 with plant metal wastes.

Various plant solutions were used to contaminate four foot by four foot panels, with and without water-soluble films applied as above. The active solutions were applied with a one inch paint brush, in some cases with the panel vertical, in others with the panel horizontal and then tipped to a vertical position to allow the excess solution to drain off. About 50 cc. of solution were applied to a 3 1/2 foot by 3 1/2 foot area. These solutions dried completely within two hours, and the activities of the panels were then determined by taking electroscope readings at the center of the panel with the electroscope case in a standard position either one inch or three inches from the panel. Electroscope readings were also made at other positions on the panel, but those in the center were consistent and showed the largest differences before and after washing. After periods ranging from two to eighteen hours following application of the active solutions, the films were washed off in the manner described



above, and the panel activities again determined. Background activities were then determined, after substituting an unused panel for the panel tested.

The results of the tests are shown in Table C. With plant 11M solution, obtained by dissolving neutron irradiated uranium slugs in nitric acid, a decontamination factor of 118 was obtained, compared to 15 without protection by any water-soluble film. With the tapioca starch dextrin-CaCl<sub>2</sub> films, all panel activities, after washing, were equal to or less than 1 mr./hr. at three inches. Four to six coats are therefore adequate, and may be more than are actually required.

Table C

| No.    | Tapioca starch dextrin-CaCl <sub>2</sub> Film                                  | Active Solution Used  | Electroscope Readings 3" from Panel* |         |               |         | Decontamination Factor | Remarks |
|--------|--|---|--------------------------------------|---------|---------------|---------|------------------------|---------|
|        |  |   | Contaminated                         |         | After Washing |         |                        |         |
|        |  |   | Div./Min.                            | Mr./Hr. | Div./Min.     | Mr./Hr. |                        |         |
| 1..... | None.....  | Plant 11M (dissolver solution), dried 2 hours.                      | 176                                  | 61      | 62            | 21      | 2.8                    |         |
| 2..... | 1% wetting agent solution added b; 6 coats, dried 2½ days.                     | Plant 11M, dried 18 hours....                                       | 272                                  | 103     | 2.3           | 1       | 118                    | Note 1. |
| 3..... | 4 coats, dried 5 days.....   | Plant 23MS (metal waste), dried 2 hours.                            | 130                                  | 45      | 2.7           | 1       | 48                     | Note 2. |
| 4..... | 4 coats.....   | Na <sub>2</sub> CO <sub>3</sub> -neutralized Plant 23MS, pH=ca. 12. | 50                                   | 17      | 0             | 0       | ∞                      | Note 3. |
| 5..... | ½% wetting agent solution added b; pH to 6.8 with HCl; 6 coats, dried 1½ days. | Plant 53WS (decontamination waste), dried 2½ hours.                 | 31                                   | 10      | 0.9           | 0.3     | 34                     | Note 4. |

\* Corrected for background readings, which were 0.5 to 1 div./min.  
b Commercial sulfated higher alcohol type shampoo solution.  
Note 1.—This contaminated panel stood overnight at high humidity, and moisture condensed on the panel and dripped off, yet excellent decontamination was obtained.  
Note 2.—Wash was for only 21 minutes instead of 31 minutes.  
Note 3.—Wash was ½ minute H<sub>2</sub>O on, 2 minutes soak, instead of 1 minute on, 4 minutes soak.  
Note 4.—Activity measured one inch from panel instead of three inches.

It has been found that for low humidity areas, such as areas wherein the relative humidity is up to about 30%, glycerine containing films are particularly advantageous for use as a protective coating, whereas glycerine-free films are particularly advantageous for areas having comparatively high humidity, for example above 30% relative humidity.

While our invention has been described with reference to certain particular embodiments and with reference to certain specific examples, it is to be understood that the invention is not to be limited thereby. Therefore, changes, omissions, and/or additions may be made without departing from the spirit of the invention as defined in the appended claims, which are to be limited only as required by the prior art.

We claim:

1. A process for protecting and decontaminating a surface which is subject to radioactive contamination which comprises coating said surface, prior to contamination thereof, with a coating material comprising a water-soluble carbohydrate, a hygroscopic metal halide, and water, and, subsequent to contamination of the resulting coated surface, removing said coating and the radioactive contamination associated therewith by washing with water.

2. A process for protecting and decontaminating a surface which is subject to radioactive contamination which comprises coating said surface, prior to contamination thereof, with a coating material comprising a water-soluble carbohydrate, a hygroscopic metal halide, a water-soluble plasticizer, and water, and, subsequent to contamination of the resulting coated surface, removing said coating and the radioactive contamination associated therewith by washing with water.

3. A process for protecting and decontaminating a surface which is subject to radioactive contamination which comprises coating said surface, prior to contamination thereof, with a coating material comprising 15-25 parts by weight of a starch dextrin, 5-15 parts by weight of a hygroscopic metal halide, and 70-80 parts by weight of

water, and, subsequent to contamination of the resulting coated surface, removing said coating and the radioactive contamination associated therewith by spraying said surface with water.

4. A process for protecting and decontaminating a surface which is subject to radioactive contamination which comprises coating said surface, prior to contamination thereof, with a coating material comprising 15-25 parts by weight of a starch dextrin, 5-15 parts by weight of a hygroscopic metal halide, up to 5 parts by weight of a polyhydric alcohol, and 70-80 parts by weight of water, and, subsequent to contamination of the resulting coated

surface, removing the coating and the radioactive contamination associated therewith by spraying said surface with water.

5. A process for protecting and decontaminating a surface which is subject to radioactive contamination which comprises coating said surface, prior to contamination thereof, with a coating material comprising 15-25 parts by weight of tapioca starch dextrin, 5-15 parts by weight of calcium chloride, and 70-80 parts by weight of water, and, subsequent to contamination of the resulting coated surface, removing the coating and the radioactive contamination associated therewith by intermittently spraying said surface with water.

6. A process for protecting and decontaminating a surface which is subject to radioactive contamination which comprises coating said surface, prior to contamination thereof, with a coating material comprising 15-25 parts by weight of tapioca starch dextrin, 5-15 parts by weight of calcium chloride, up to 5 parts by weight of glycerine, and 70-80 parts by weight of water, and, subsequent to contamination of the resulting coated surface, removing said coating and the radioactive contamination associated therewith by intermittently spraying said surface with water.

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