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COMPOSITIONS AND PROCESS FOR REMOVAL OF RADIOACTIVE CONTAMINANTS

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This invention relates to the decontamination of surfaces on which are deposited radioactive materials, and is especially concerned with a novel composition and process for the removal of radioactive elements from surfaces such as metals, concrete, porcelain, and such other organic and inorganic surface materials that are commonly used in conjunction with the purification, production, or utilization of radioactive isotopes.

In the production and utilization of radioactive isotopes, the processing equipment becomes contaminated through precipitation of the radioactive ingredients being processed or by irradiation of the materials of which the equipment is constructed. Frequently this equipment must be disassembled and repaired or replaced, and the radiation levels are so high that they constitute a health hazard to any workmen approaching the area. In such instances, it is necessary to replace the equipment completely, permit the radioactive isotopes to degenerate to a stable state through a natural process of decay, or remove the contamination by some cleaning process.

In other instances, areas are contaminated inadvertently through the medium of spillage, equiment breakage, or radioactive dust.

In still other instances, radioactive materials tend to build up through natural processes such as concentration in plants or animals, e.g. algae or plankton, so that continued deposition of these bodies in a given locality may concentrate radioactive isotopes to such an extent that they become a health hazard.

One such instance of the latter class of contamination consisted of a high concentration of radioactivity produced through the deposition of plankton from river water, which river water carried the effluent from an isotope production facility. The plankton absorbed the small amounts of radioactive isotopes as body building materials, such as phosphorus 32, and when recirculated later through cooler or condenser tubes tended to deposit and die on the heated surface of the condenser tubes. The tubes were an integral part of an atomic reactor for the production of radioactive isotopes. The tubes were constructed of aluminum and other components of the cooling system were fabricated from stainless steel. Ultimately, the concentration of radioactive isotopes produced through the deposition of plankton on the condenser tubes formed a health hazard for workmen who were required to repair or replace these tubes.

The components of the radioactive material deposited from the plankton were known to be principally beta-gamma emitters, that is, such plankton had absorbed radioactive fission products and soft beta radiation emitters giving off beta and gamma rays. For testing purposes, a number of sections of the exchanger tubes were removed from the pile and cut into convenient sections. Reagents of conventional type were tested for decontamination effectiveness by contacting the aluminum sections for various periods of time with these reagents.

In the past, it has been known to use such reagents as hexametaphosphate, citric acid, tartaric acid, nitric acid, chromic acid, the sodium salt of ethylene diamine tetraacetic acid, and the like, for the removal of such radioactive materials. These reagents were tested for decontamination of the above pipe sections and were found to be practically ineffective. Certain of these reagents also

possess other inherent undesriable properties. Thus, in the case of chromic acid, for example, not only was this material substantially ineffective, but posed the additional problem of the disposal of large volumes of radioactive effluent containing high concentrations of chromium as chromate ion after decontamination.

It is an object of this invention to provide a commercially available, inexpensive composition, and a simple, rapid, efficient process for the removal of radioactive materials from surfaces of metals, concrete, porcelain and the like.

A further object is to provide a composition and process for the removal of radioactive materials by solution or dispersion in a liquid reagent of a type permitting convenient removal and rinsing of such materials, and subsequent treatment of the liquid reagent for convenient disposal thereof.

A further object of the invention is to provide a composition and process for dissolution, chelation, or sequestration of the radioactive isotopes in such a form that the dissolved compound, chelate, or sequestrate readily can be decomposed or converted to an insoluble form to prevent subterranean leaching or release of the radioactive material.

A still further object is the provision of a composition for the above purpose, which is relatively non-toxic to personnel or to animal or plant life so that the composition may be disposed of safely in streams or subterranean basins.

I have found that an aqueous acid solution containing sulfamate ions is effective for removal of radioactive contaminants from surfaces, such as the surfaces of metallic condenser tubes of atomic reactor installations. Of particular significance I have found that an aqueous solution containing sulfamate, halogen and hydrogen ions is markedly effective, and is much more effective in this respect than any of the prior art radioactive decontaminating compositions. It is believed that the combination of sulfamate and halogen ions in acid solution at the proper pH, pointed out more fully hereinafter, function in a synergistic manner to achieve effective removal of radioactive contaminants according to the invention.

While the invention is not to be taken as limited by any theory of the operation of my above noted solutions, it is believed that the presence of the sulfamate ion, and particularly sulfamate ion in combination with halide ion brings about effective dissolution or suspension of the radioactive isotopes, thus removing them from the surface being treated. Such radioactive isotopes may be in the form of a dissolved compound or complex produced by interaction of such isotopes with the ions of my solution, such as the sulfamate and halide ions, or the isotopes may be in the form of a chelate or sequestrate in my solution as result of interaction with the sulfamate and halogen ions. At present, however, I am not aware of the actual manner in which my solution functions to effectively remove radioactive contamination from surfaces.

However, the complex or dissolved compound containing the radioactive istotopes formed in my solution is relatively unstable, and the sulfamate with which these isotopes are associated in one form or another, can be hydrolized or decomposed to other products. For example, such complex or dissolved compound can be rendered insoluble by maintaining the acid solution thereof at elevated temperature for an extended period of time, or by reaction with nitric acid, or both, to produce precipitates such as insoluble sulfate or bisulfate salts with which the radioactive contaminants are bound, so

that these contaminants can be effectively removed from solution. These reactions may be illustrated as follows:

$$XSO_3NH_2 + H_2O \xrightarrow[\text{heat}]{\text{acid}} XHSO_4 + NH_3$$

$$2XSO_3NH_2 + 2H_2O \xrightarrow[\text{heat}]{\text{acid}} X_2SO_4 + (NH_4)_2SO_4$$

$$XSO_3NH_2 + HNO_3 \longrightarrow XHSO_4 + H_2O + N_2O$$

where X is a radioactive metallic ion such as the radioactive rare earth metals. It is understood that the above equations are merely illustrative and are not intended to indicate the exact nature of the actual reactions involved.

To provide the sulfamate ion, I may employ any water soluble sulfamate or sulfamic acid, preferably the latter, since it also simultaneously produces the hydrogen ion required to obtain the proper acidity or pH. I can also use mixtures of sulfamic acid and sulfamates. Where sulfamate salts are employed these can be alkali metal, e.g., sodium or potassium, or ammonium sulfamates, or other inorganic sulfamates that are soluble in a concentration at least within the broad range noted below, and which ionize to produce sulfamate ions in acid media without producing undesirable precipitates in acid media or with the radioactive elements being removed. The sulfamic acid or sulfamates can be employed in a concentration or proportion of as low as about 0.03% and as high as about 10% by weight of the solution, although such range is not to be considered critical. In preferred operation, I employ a concentration of sulfamic acid or sulfamate of from about 0.4% to about 5% by weight of the solution.

Any soluble halide, e.g., chloride or fluoride can be utilized. Thus, for example, the alkali metal, such as sodium or potassium, chloride or fluoride, or the ammonium chloride or fluoride can be used. The halide preferably used is the fluoride ion, and a particularly useful fluoride is the alkali metal or ammonium bifluorides (acid fluorides) such as ammonium bifluoride (NH_4HF_2). These halides may also be employed in admixture with each other, and I have found that the use of a combination of fluorides with other halide ions, preferably chloride, such as a combination of sodium chloride and ammonium bifluoride, are particularly effective in conjunction with the sulfamate ion producing material, especially sulfamic acid. Thus, for example, I have found that a solution of sulfamic acid, sodium chloride and ammonium bifluoride produce outstanding decontamination results, as pointed out more fully hereinafter. It is believed that the incorporation of the above fluoride together with the sodium chloride in the aforementioned solution aids in dissolving a portion of the surface oxide coating on a metallic surface such as aluminum, and in which surface coating the radioactive elements are believed concentrated, thus facilitating decontamination. Further, the acidic nature of the bifluoride aids in producing the required pH of solution as described below. The amount of halide employed in the solution may vary. For example, I may use an amount of halide to sulfamate or sulfamic acid in a proportion of about 10 to 90 parts of sulfamic acid or salt of sulfamic acid to about 10 to 90 parts of halide.

It has been found that in order to produce effective decontamination, the solution containing sulfamate and halogen ions should also contain a sufficient concentration of hydrogen ions so that the solution has a pH not greater than about 3, and in preferred operation not greater than about 1.5. The use of sulfamic acid for this purpose is particularly preferred and is economical since this material furnishes the required sulfamate ion and at the same time is a strong acid which may also supply sufficient concentration of hydrogen ion to produce the low pH within the aforementioned range. In this case an additional hydrogen ion producing material may be unnecessary. However, where a sulfamate salt is employed or where the amount of sulfamic acid used is insufficient

to afford the desired acidity, an additional hydrogen ion producing material is employed. Such additional material may be an acidic substance such as hydrochloric acid, dilute sulfuric acid of less than 70% concentration or an acid salt such as ammonium bifluoride, ammonium bisulfate or sodium diacetate, provided such acidic substances do not react with the sulfamic acid or sulfamate to precipitate the latter materials out of solution, or to form deleterious reaction products therewith.

The addition of surface active agents to the aqueous acid solution of the invention improves the effectiveness of such solution. By the term "surface active agent" I mean those compounds which are characterized by an appreciable reduction in surface tension of water when used in small quantities in aqueous solution or dispersion and which are known to be useful as wetting agents, detergents, penetrating agents, emulsifying agents, and the like. The molecule of the surface active agent is characterized by highly polar ionic materials such as cationic surface active agents and non-ionic materials such as characterized by the well known non-ionic surface active agents and further by relatively high molecular weight of these materials which possess groupings which are highly hydrophobic on one end of the pole and highly hydrophilic on the other. For this purpose I may employ, for example, cationic or non-ionic surface active agents, preferably the latter. The cationic or non-ionic surface active agents which I employ are those which are stable chemically in acid solutions at a pH of 3 or less. Specific illustrative examples of suitable non-ionic surface active agents which I may employ are alkylarylpolyether alcohols, marketed as Triton X–100, polyoxyethylene sorbitan monolaurate, marketed as Tween 21, and polyoxyethylene lauryl ether, marketed as Brij 35. Specific examples of suitable cationic surface active agents are the fatty acid tertiary amines marketed as Ethomeen, and particularly the quaternary ammonium compounds such as the alkyl dimethyl benzyl ammonium chlorides, e.g., Roccal, and diisobutyl (p-tert. cetyl) phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, such as Hyamine 1622. The amount of surface active agent employed may vary over wide ranges, but generally about 0.001 to about 0.2% by weight of the solution is used.

The surface active agent is employed in my composition to aid in removing non-radioactive oily materials such as fats and greases so that the decontamination compound can more readily dissolve the radioactive materials, to improve the rate of penetration of the decontamination composition so that the time of decontamination is reduced, and to permit the aqueous decontamination composition to more readily wet the surface being decontaminated in order to more rapidly and completely effect the decontamination or removal of the radioactive materials from such surface. However, it is to be understood that the surface active agent is not an essential component of my composition, and may be omitted therefrom if desired.

In formulating the acid aqueous solution of the invention, I may mix together the ingredients in concentrated or dry form, for example, the sulfamic acid or sulfamate compound, the halide or mixtures thereof, the additional acidic compound, when employed, and also the surface active agent, if used, to form a single composition which can be packaged and when ready for use, added to water. If desired, however, the ingredients may be separately dissolved in water to give the solutions of the invention.

In the above concentrated or dry compositions the amount of sulfamic acid or sulfamate present may range from about 10% to about 90% by weight of said composition, and the ratio of sulfamic acid or sulfamate compound to halide can vary from about 10 parts by weight of such compound to about 90 parts halide, to about 90 parts of sulfamic acid or sulfamate to about 10 parts of

halide. The concentrated or dry composition of the above type can be added to water in an amount generally ranging from about ½ to 10 ounces, usually about 1 to 7 ounces, per gallon of solution, depending particularly on the amount of sulfamic acid or sulfamate contained in the concentrate or solid mixture of ingredients. The amount of such mixture added to water is such as to produce an acid solution having a pH within the range noted above, that is, a pH not greater than about 3.

Small amounts of other materials which do not affect the functioning of the main ingredients of my composition for removal of radioactive contamination, may be present in the compositions or solutions of the invention, such as small amounts of materials usually associated as impurities with the main ingredients, such as sulfates present with the sulfamates. Further, other ions such as sulfate, phosphate or acetate may be added in conjunction with hydrogen ion forming materials to supply the necessary acidity without materially affecting the decontamination properties of the composition.

The acid solution of the invention used for decontamination of surfaces containing radioactive elements or emitters, can be applied to the surface at normal or at elevated temperatures, e.g., up to 100° C. or more. Greater effectiveness, that is, a greater percentage of decontamination, is usually realized at the elevated temperatures. Contact time of the solution with the surface being decontaminated will vary with such factors as composition of the solution, temperature thereof, type of material undergoing treatment, the percentage of decontamination desired, etc. It is preferred to obtain as large a measure of decontamination per surface area as is possible in a relatively short period of treatment by the solution, say on the order of about 5 minutes. Following treatment of the contaminated surface with the acid solution, the spent solution can be conducted to another zone, and therein treated to precipitate the sulfamate and the radioactive elements associated therewith, e.g., by heating the aqueous solution, treating with nitric acid, or both, for a sufficient period of time, or by other means well known in the art for decomposition of sulfamates. The precipitate can then be removed, e.g., by filtration or concentration, and the recovered solids then conveniently disposed of or treated to recover the radioactive isotopes.

The tests on removability of radioactive contamination according to my invention were conducted on sections of aluminum heat exchanger tubes removed from an atomic reactor pile assembly. A determination of the level of beta-gamma radiation from a unit surface area was made before treatment with the acid solutions and after such treatment. The materials emitting beta and gamma rays were included in a single category because the counting devices determined the radiation level of both of these rays together. The materials emitting such rays were believed to be fission products and soft beta emitters. The percentage of decontamination reported in each case was the value obtained from the following formula:

$$100\left(1-\frac{\text{counts after treatment}}{\text{counts before treatment}}\right)$$

In Example 1 below is given a series of compositions which were each added to water at a concentration of 6 ounces per gallon of solution, and each of the resulting solutions except D' was employed for treatment of the aluminum condenser tube sections for a period of 5 minutes at temperatures of 22° C. and 80° C. respectively. Composition D was also tested at 50° C. Composition D' was tested at 50° C. and 80° C.

EXAMPLE 1

Composition—ingredients	Percent by weight	Percentage of decontamination at 22° C.	Percentage of decontamination at 50° C.	Percentage of decontamination at 80° C.	pH of Aqueous Solution
A. sulfamic acid	10	0		42	1.4
ammonium chloride	90				
B. sulfamic acid	50	15		48	0.8
sodium chloride	50				
C. sulfamic acid	10	20		62	2.4
ammonium chloride	80				
ammonium bifluoride	10				
D. sulfamic acid	50	47	97	99	1.5
sodium chloride	40				
ammonium bifluoride	10				
D'. sulfamic acid	50		99	99	1.4
ammonium bifluoride	50				
E. ammonium chloride	90	0		9	4.0
sodium nitrate	10				
F. ammonium chloride	80	14		20	4.6
sodium nitrate	10				
sodium diacetate (50% sodium acetate and 50% acetic acid	10				

From the above data it is noted that by increasing the amount of sulfamic acid from 10% in compositions A and C, to 50% in compositions B and D, corresponding to an increase in concentration of the sulfamic acid in the corresponding solutions of from about 0.45% in the case of solutions formed from compositions A and C, to about 2.25% by weight of the solution formed from compositions B and D, an improvement in decontamination was achieved. Of particular note it is seen that when 10% of the ammonium chloride of composition A was replaced by 10% of ammonium bifluoride as in composition C, and when 10% of the sodium chloride of composition B was replaced by 10% of ammonium bifluoride as in composition D, an outstanding improvement in decontamination effectiveness was obtained. This is particularly noted in the case of composition D wherein 97% and 99% decontamination was achieved at 50° C. and 80° C., respectively, giving practically complete decontamination under these conditions. It is also particularly noteworthy that composition D' containing 50% sulfamic acid and 50% ammonium bifluoride gives practically complete decontamination of 99% at both 50° C. and 80° C. This clearly shows the effectiveness of employing a fluoride, or a mixture of fluoride and chloride, in combination with sulfamate in the acid solution according to the invention. Compositions D and D' are preferred formulations.

It is also noted that in contrast to the above solutions and compositions A to D' containing sulfamic acid, the solutions formed from compositions E and F containing alkali metal halide without sulfamate were in most instances comparatively greatly inferior in radioactive decontamination effectiveness, especially under treatment at elevated solution temperatures of 80° C. Thus, for example, by replacing the 10% sodium nitrate in composition E with 10% sulfamic acid as in composition A, decontamination at 80° C. was increased from 9% to 42%, and by replacing the 10% sodium nitrate and 10% sodium diacetate of composition F with 10% sulfamic acid and 10% additional of ammonium chloride as in composition A, decontamination at 80° C. was more than doubled from 20% for composition F to 42% for composition A, and by replacement of such sodium nitrate and sodium diacetate with 10% sulfamic acid and 10% ammonium bifluoride as in composition C, decontamination at 80° C. was about tripled from 20% to 62% for composition C.

EXAMPLE 2

Tests using the same procedure as noted above were carried out employing composition D above, one of said tests (*a*) being carried out using a concentration of one ounce per gallon of solution of composition D, the contact time being 5 minutes, and a second test (*b*) carried

out using a concentration of 0.1 ounce of composition D per gallon of solution, with a contact time of 15 minutes, the solutions in both tests being maintained at 80° C. In test (*a*) 66% decontamination was realized and in test (*b*) 24% decontamination was obtained. These tests show that even at the low concentration of about 0.4% and .04% sulfamic acid by weight of the solution employed in tests (*a*) and (*b*), respectively, the sulfamic acid solution of the invention has a superior degree of effectiveness for decontamination of radioactive materials as compared to prior art formulations.

EXAMPLE 3

The following compositions dissolved in water according to the procedure of Example 1 and each applied in the manner described in Example 1 at a concentration of 6 ounces per gallon and 10 ounces per gallon will also show improved radioactive decontamination effectiveness as in the case of compositions A to D'.

Composition—Ingredients in Percent by Weight

G. Sodium sulfamate	80
Hydrochloric acid (dry basis)	20
H. Ammonium sulfamate	40
Sulfamic acid	20
Sodium chloride	40
I. Sulfamic acid	50
Sodium fluoride	50
J. Ammonium sulfamate	30
Sulfamic acid	20
Sodium chloride	40
Ammonium bifluoride	10

Compositions I and J containing sodium fluoride and ammonium bifluoride, respectively, are more effective than compositions G and H not containing a fluoride.

EXAMPLE 4

The following compositions K and L, which are similar to compositions B and D, respectively, but in addition contain small amounts of surface active agents as described below, when dissolved in water according to Example 1 and applied in the manner of Example 1 also show marked effectiveness for radioactive decontamination similar to that for the solutions formed from compositions B and D.

Composition—Ingredients in Percent by Weight

K. Sulfamic acid	50
Sodium chloride	48
Wetting agent (Triton X–100)	2
L. Sulfamic acid	50
Sodium chloride	39
Ammonium bifluoride	10
Wetting agent (Roccal)	1

The addition of the surface active agents to compositions B and D, forming compositions K and L, enhanced the effectiveness of the compositions B and D, mainly in reducing the time required to produce the same degree of decontamination.

EXAMPLE 5

The solution formed in Example 1 from composition D was tested in a manner similar to Example 1 on stainless steel contaminated with plutonium, a material emitting alpha radiation, as contrasted to the beta-gamma emitters found in the above noted condenser tubes. When employed at ambient temperature, such solution effected a 99% decontamination of the steel. This indicates that my sulfamate and halide-containing acid solution is highly effective in decontamination of radioactive materials emitting alpha rays as well as for materials emitting beta and gamma rays.

EXAMPLE 6

The solution formed in Example 1 from composition D was tested for decontamination of concrete on which spillage of beta-gamma emitting fission products had produced a high degree of radio activity. It was found that such solution decontaminated the concrete surface to a low level such that it did not present a personnel hazard, such solution tending to penetrate the concrete and thereby removing the radiation emitting materials from the pores thereof. It is noteworthy that heretofore, to my knowledge, it was most difficult to effectively decontaminate concrete containing radioactive radiation emitters.

From the foregoing, it is seen that my aqueous acid solution containing sulfamate and halogen ions, is much more effective than compositions previously known for decontaminating and removing radioactive materials from surfaces. My compositions and procedure employing same also possess the advantages of alleviating or minimizing waste disposal problems. Further, the ingredients or components of my composition are inexpensive, readily available and present practically no difficulty or hazards in formulation and handling.

While I have described particular embodiments of my invention for the purpose of illustration, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention as set forth in the appended claims.

I claim:

1. A solid composition of matter for removal of radioactive contaminant from surfaces, consisting essentially of about 10 to about 90% by weight of said composition, of a compound of the group consisting of sulfamic acid and water soluble salts of sulfamic acid, and a water soluble fluoride, the ratio of said compound to said fluoride, ranging from about 10 parts by weight of said compound to about 90 parts fluoride, to about 90 parts of said compound to about 10 parts of said fluoride, said composition when dissolved in water giving a sulfamate ion, a fluoride ion, and a hydrogen ion.

2. A composition of matter for removal of radioactive contaminants from surfaces as defined in claim 1, wherein said compound is sulfamic acid and including a water soluble chloride, the ratio of said compound to total halide ranging from about 10 parts by weight of said compound to 90 parts of halide, to about 90 parts of said compound to about 10 parts of halide, said halide consisting of a substantial proportion of said fluoride.

3. A composition of matter for removal of radioactive contaminants from surfaces as defined in claim 1, wherein said compound is sulfamic acid, and said fluoride is ammonium bifluoride, and including sodium chloride.

4. A composition of matter for removal of radioactive contaminants from surfaces as defined in claim 1, wherein said compound is sulfamic acid, and said fluoride is ammonium bifluoride.

5. An aqueous acid solution for removal of radioactive contaminants from surfaces, consisting essentially of from about .03% to about10% by weight of said solution of a compound of the group consisting of sulfamic acid and water soluble salts of sulfamic acid, and a water soluble fluoride, the amount of said compound to fluoride being in a proportion of about 10 to 90 parts of said compound to about 10 to 90 parts of said fluoride, said composition furnishing in said solution a sulfamate ion, a fluoride ion, and a hydrogen ion, said solution having a pH not greater than about 3.

6. An aqueous acid solution as defined in claim 5, wherein said compound is sulfamic acid, and including a water soluble chloride, and the sulfamic acid is present in an amount of about 0.4% to about 5% by weight of said solution.

7. A process for removal of radioactive contaminants from a surface, which comprises treating said surface with an aqueous acid solution consisting essentially of

sulfamic acid and ammonium bifluoride, said solution having a pH not greater than about 1.5, the sulfamic acid being present in an amount of about 0.4% to about 5% by weight of said solution.

8. A process for removal of radioactive contaminants from a surface, which comprises treating said surface with an aqueous acid solution consisting essentially of sulfamic acid and a water soluble inorganic halide of the group consisting of alkali metal and ammonium chlorides, fluorides, and bifluorides, said solution having a pH of about 1.5, the sulfamic acid being present in an amount of about 0.03% to about 10% by weight of said solution.

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