

**Abstract**

The invention relates to a radioactive package for ground-level or underground geological storage comprising radioactive waste and a first layer of vitrified materials, and a blocking layer comprising a matrix based on liquefied thermoplastic materials comprising a mixture of thermoplastic materials micronised to between 400 and 700 microns and preferably to 500 microns, and an iron oxide powder micronised to between 80 and 250 microns. The invention also relates to the blocking layer and to a method for securing a radioactive waste package.

**We claim:**

1. A radioactive package for ground-level or underground geological storage comprising radioactive waste and a first layer of vitrified materials, and a blocking layer comprising a matrix based on liquefied thermoplastic materials comprising a mixture of thermoplastic materials micronised to between 400 and 700 microns and preferably to 500 microns, and an iron oxide powder micronised to between 80 and 250 microns.
2. A radioactive package intended for ground-level or underground geological storage according to claim 1, characterised in that the blocking layer comprises a mixture of thermoplastics materials and iron oxide powder of the order of 60% plastics materials and 40% iron oxides.
3. A radioactive package according to claim 1 or claim 2, characterised in that the radioactive waste package furthermore comprises a protective layer of liquefied thermoplastics materials.
4. A radioactive package according to claim 3, characterised in that the protective layer has thickness of 2 to 3 mm.
5. A radioactive package according to any one of claims 1 to 4, characterised in that the blocking layer comprises packaging waste, plastics casings of all kinds, of low or high density.
6. A radioactive package according to any one of claims 3 to 5, characterised in that the protective layer comprising a mixture of liquefied polymer originates from the mixture of plastics materials micronised to 400 and 700 microns, preferably to 500 microns, dissolved in a first low-temperature step with the assistance of pinene-acetone solvents and in a second solubilisation step at a temperature of up to 160°C.
7. A method for securing a radioactive waste package, characterised in that a blocking layer comprising a mixture of liquefied thermoplastics materials micronized to 400 and 700 microns, preferably to 500 microns, and an iron oxide powder micronized to between 80 and 250 microns is applied onto a layer of vitrified materials of a radioactive package.

8. A method for securing a radioactive waste package according to claim 7, characterised in that the layer comprises a mixture of thermoplastics materials and of iron oxide powder of the order of 60% plastics materials and 40% iron oxides.
9. A method for securing radioactive waste according to claim 7 or 8, characterised in that a protective layer of liquefied plastics materials is applied onto the blocking layer.
10. A method for securing radioactive waste in which sludges originating from the recycling of plutonium and uranium are mixed with a liquefied mixture of thermoplastic materials micronised to 400 and 700 microns, preferably to 500 microns, and an iron oxide powder micronised to between 80 and 250 microns, homogenised, coated with a liquid polymer composition and then cast in stainless steel drums.
11. A method according to any one of claims 7 to 10, characterised in that the liquefied polymer originates from the polymers micronised to 500 microns dissolved in a first low-temperature step with the assistance of pinene-acetone solvents and in a second solubilisation step heated to a temperature of up to 160°C.
12. A method according to any one of claims 7 to 11, characterised in that the mixture of plastics materials and iron oxide powder comprises of the order of 60% plastics materials and 40% iron oxides.
13. A method for securing concrete serving to isolate waste from nuclear power station dismantling, in which between 50 and 120 kg/m<sup>3</sup> of concrete of a liquefied mixture of thermoplastic materials micronised to between 400 and 700 microns and an iron oxide powder micronised to between 80 and 250 microns, are mixed with the other ingredients of the concrete.

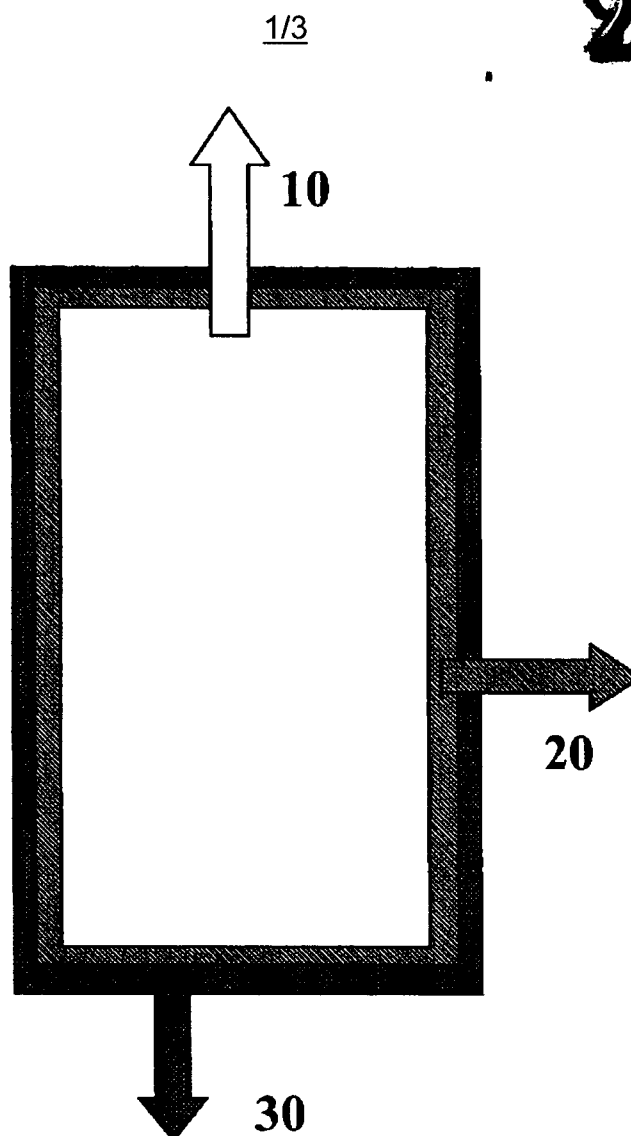
Dated this 9<sup>th</sup> day of April, 2012.



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**Figure 1**

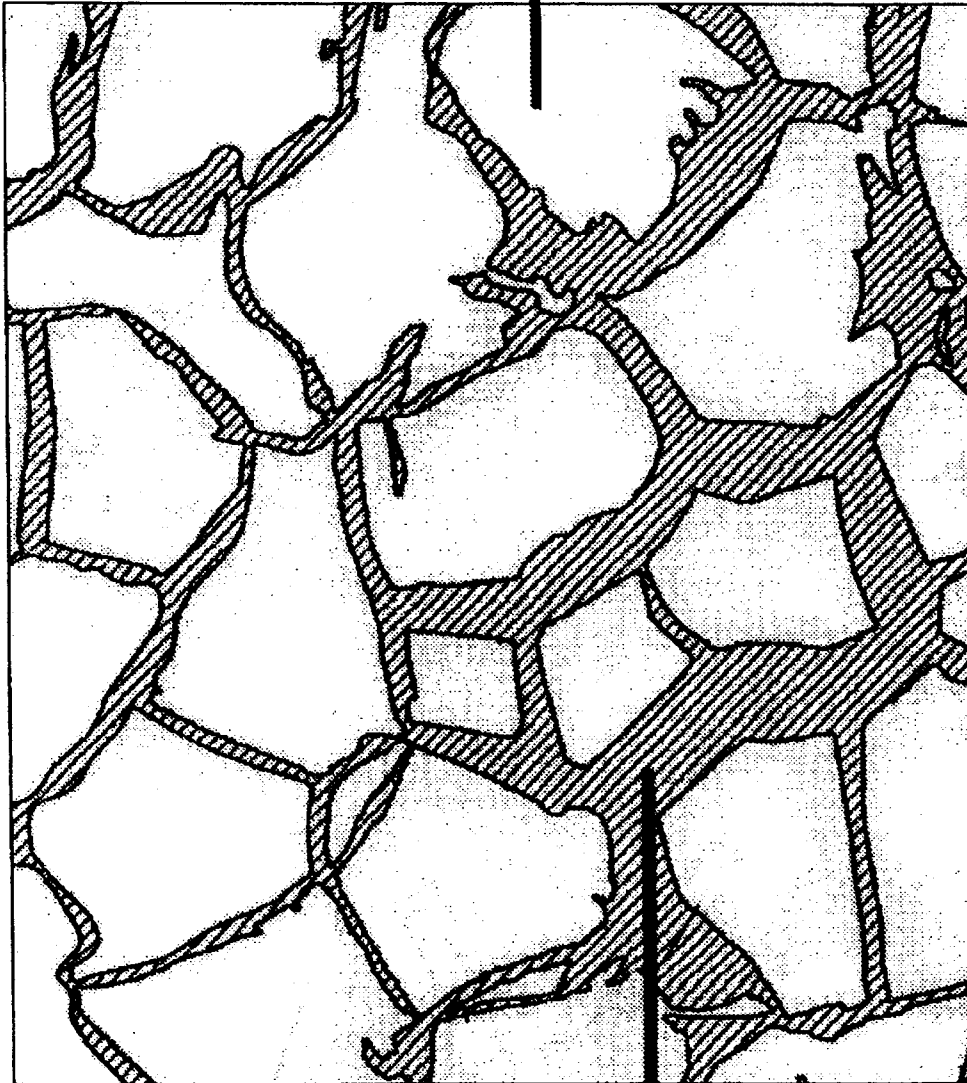
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**Figure 2**

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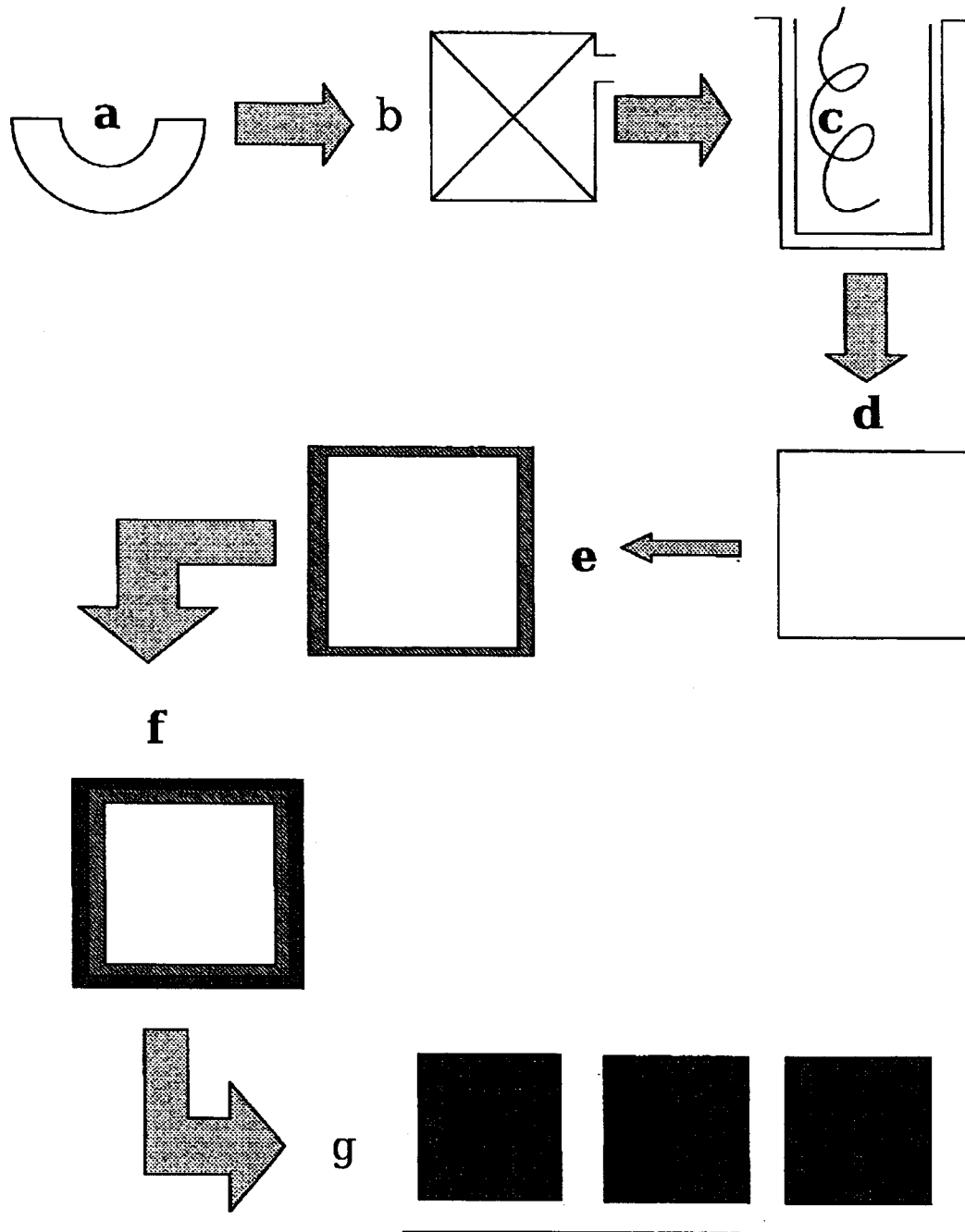


Figure 3

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## **METHOD FOR SECURING THE STORAGE OF LONG-LIVED RADIOACTIVE WASTE**

### **Field of the invention**

[0001] The present invention relates to secured radioactive packages and to a method for securing the storage of radioactive waste.

### **Background of the invention**

[0002] Natural radioactivity has been present since the "birth" of our universe; radioactivity is of cosmic (the stars, the sun) and terrestrial (uranium, thorium) origin. It is found in granite which produces a natural radioactive gas, radon, in construction materials, in water, in the air and foodstuffs, and even in our bodies (potassium 40). Exposure to natural radioactivity is not the same everywhere. It increases in particular as a function of altitude and varies as a function of local geology.

[0003] Radioactive waste is defined as any radioactive material which cannot be either recycled or reused.

[0004] Nuclear waste is of many and different origins and kinds. It includes, for example, elements present in the spent fuel from nuclear power stations, apart from the uranium and plutonium present in such fuel, radioactive elements for medical or industrial use, or materials which have been in contact with radioactive elements.

[0005] The risk presented by such materials may be assessed on the basis of two parameters:

- Radioactivity gives rise to the toxicity of the waste including its potential impact on man and the environment.
- The lifetime of the waste makes it possible to define the duration of the potential harm it may cause.

[0006] 90% of radioactive waste is low activity, "short-lived" waste. A decision as to the manner of managing such waste was made some decades ago and resulted in the construction, on an industrial scale, of ground-level storage facilities.

[0007] As for the remaining 10%, medium- or high-activity "long-lived" waste, no decision has yet been made regarding long-term management. It is today stored industrially at ground level, in complete safety and for several decades, in specially designed buildings on the sites where the waste is produced.

[0008] Waste management is defined as follows:

[0009] Advanced separation and transmutation of waste with the aim of sorting and transforming certain types of long-lived waste into other less toxic, shorter-lived types of waste. This approach makes it possible to reduce the long-term harmfulness of the waste.

[0010] Storage in a deep geological formation with the aim of developing defined underground storage facilities and technologies with reversible approaches being favoured.

[0011] Methods for packaging and long-term ground-level or underground storage, the aim of which is to develop radioactive waste packages and long-term storage procedures for them, while ensuring protection of humans and the environment with solutions which are complementary to those already in existence, so ensuring still more secure waste storage.

[0012] The main producers of waste are: (see table A in appendix 1/2)

[0013] This diagram illustrates the origin of the volumes of radioactive waste packages of all categories (low to high radioactivity, short-lived to long-lived).

[0014] Radioactive waste is classified on the basis of two criteria.

[0015] a) Its activity, namely the number of nuclear disintegrations which occur within it each second. Activity is measured in becquerels (1 Bq = 1 disintegration per second) for a mass of 1 kg of the substance.

[0016] Some examples are given below:

1 kg of rainwater:

of the order of 1 Bq (natural radioactivity)

1 kg of granitic soil:

of the order of 10,000 Bq (natural radioactivity)

1 kg of uranium ore:

of the order of 100,000 Bq (natural radioactivity)

1 kg of recently unloaded spent fuel\*:

of the order of 100,000,000,000,000 Bq.

[0017] \*Activity falls over time. After 10 years, the activity of spent fuel has fallen approximately by a factor of 6.

[0018] b) Its radioactive decay period or "half-life" is by definition the time required for a substance's activity to reduce by half.

[0019] The radioactive half-life does not depend on the mass of material in question. Each pure radionuclide has a precisely known half-life, the value of which may range from less than a thousandth of a second (for example polonium 214: 0.16 ms) to several billion years (for example uranium 238: 4.5 billion years) and all points between (iodine 131: 5 days, caesium 137: 30 years, plutonium 239: 24,000 years, uranium 235: 7 million years, etc.).

[0020] If the substance is mixed, the radioactive half-life is taken to be the longest of the half-lives of all the radionuclides present.

[0021] A radionuclide is transformed by disintegration into another nucleus known as a "daughter product"; either this daughter nucleus is stable, or is itself also radioactive and disintegrates in turn, and so on until it forms a stable nucleus.

[0022] A short-lived initial nucleus may very well have long-lived daughter products. In this case, it is the half-life of the latter which is taken into account.

[0023] On the basis of these two criteria, activity and half-life, 8 categories may be defined into which the waste from nuclear power stations and reprocessing plants will be classified (see table B in appendix 2/2).

[0024] This table is not exhaustive; for example primary circuit filters, which are classified as "low or medium activity, short life", do not appear here.

[0025] The packaging of radioactive waste ultimately gives rise to the manufacture of what is known as a radioactive waste package or alternatively radioactive package. This radioactive package comprises radioactive waste which has been ground and selected on the basis of its radioactivity criteria. The waste is enclosed in a first layer of vitrified materials (a glass casing), which isolates the waste from any contact with humans and their environment. Depending on the particular case, the radioactive package comprises a container which blocks alpha and beta rays and a proportion of gamma rays and facilitates handling.

[0026] Radioactive waste generally originates from the items used in the operation of nuclear power stations, such as dismantling materials, gloves, overboots, tools, resin filters, metal cladding, fuel, processing residues or alternatively hospital and laboratory waste which make use of the properties of technetium, iodine or cobalt for diagnosing or treating tumours.

[0027] These various types of waste are managed in accordance with their particular characteristics: level of activity and decay period.

[0028] International patent application WO00/02855 describes materials and compositions for creating a protective shield against and for containing radioactive substances. These materials or compositions are a mixture comprising two or more organic polymers in which enclosed filler materials are subjected to crosslinking within the phenylic side chains of the polymers and copolymers. The material comprises a mixture of vulcanised rubber and/or rubbery polymer, various inclusions providing a radiation shielding effect, a polyimide resin and a phenol-formaldehyde resin. After having been mixed in appropriate proportions, the material is cured at elevated temperature (260°C).

The final material has a density of between 8 and 50 pounds per cubic foot depending on the proportion and the nature of the inclusions providing radiation resistance.

[0029] Patent application EP0055671 relates to a method for immobilising radioactive contamination on materials or waste in order to permit completely safe transfer of the materials or to package them when they have a low level of activity. According to this method, the item of contaminated material is sprayed, using an electrostatic spray gun, with at least one layer of a polymerisable resin at ambient temperature, for example an epoxy resin, a reinforced polyester resin, a vinyl resin or a mixture of thermosetting resin and thermoplastic resin.

[0030] Since water is, on the one hand, the primary factor to bring about the deterioration of radioactive waste packages, and, on the other hand, the principle vector for any radioactive elements released into the geological barrier, modelling the movement of underground water is a complex problem. Such modelling relies on Darcy's law which relates to the flow of water in a porous medium. In this type of flow, it is a pressure differential which brings about water movement, said water entraining all or part of certain elements with it. The above considerations incidentally assume that all the stored radioactive atoms are in the form of water-soluble compounds.

### **Object of the invention**

[0031] One object of the present invention is to secure radioactive packages which are intended for ground-level or underground geological storage.

[0032] According to the invention, said object is achieved by a radioactive package for ground-level or underground geological storage comprising radioactive waste and a first layer of vitrified materials, and a blocking layer comprising a matrix based on liquefied thermoplastic materials comprising a mixture of thermoplastic materials micronised to between 400 and 700 microns and preferably to 500 microns, and an iron oxide powder micronised to between 80 and 250 microns.

[0033] For the purposes of these presents, a matrix based on liquefied thermoplastic materials is taken to mean the fact of liquefying or dissolving one or more thermoplastic polymers, mixing them with the other micronised components and then resolidifying the resultant mixture. A blocking layer is thus obtained which comprises particles of thermoplastic materials micronised to between 400 and 700 microns and an iron oxide powder micronised to between 80 and 250 microns in a matrix based on liquefied thermoplastic polymer which, after solidification, binds the particles of micronised thermoplastic materials and the particles of iron powder to form a compact layer.

[0034] The object of the present invention is to isolate the waste from the biosphere until the radioactivity approaches natural concentrations, by coating the glass matrix (package) with a blocking layer comprising a matrix based on liquefied thermoplastic materials comprising a mixture of thermoplastic materials micronised to between 400 and 700 microns, preferably to 500 microns, and an iron oxide powder micronised to between 80 and 250 microns. This layer will also service as a radiation- and heat-resistant binder. Thanks to its static nature and radiation absorption capacity, this layer will block all radiation. It will be of a minimum thickness of 2 mm, preferably of 3 mm. Depending on the shape or configuration of the packages and their level of radioactivity, the thickness of the blocking layer may be as much as approximately 15 mm.

[0035] This blocking layer is inert towards water, so accordingly securing the storage of radioactive packages, which will no longer release any radioactivity in the event of incidents for hundreds of years and more, and will assist the decay of the radioactivity contained by the package.

[0036] The fact that the iron particles are very fine and well mixed into a liquefied (and then resolidified) matrix enhances their effectiveness and substantially reduces the radioactive radiation from the packages treated in this manner.

[0037] This blocking layer is preferably applied directly onto the package by a spraying method such as for example airless spray atomising equipment.

[0038] The blocking layer preferably comprises between 10% and 30% by weight of liquefied thermoplastic materials forming the matrix, 25 and 55% by weight of particles of micronised thermoplastic material and 15% and 40% of micronised iron oxide particles. In one particularly preferred embodiment, the composition of the mixture of plastics materials and iron oxide powder of the blocking layer may be of the order of 60% plastics materials and 40% iron oxides.

[0039] Onto this blocking layer, which absorbs radiation of all kinds, a protective layer of liquefied plastics of a thickness of 2 to 3 mm is advantageously applied.

[0040] After drying, the protective layer protects the blocking layer and prevents infiltration of water.

[0041] The plastics materials used advantageously originate from packaging waste or plastics casings of all kinds which are not recycled by the injection moulding or recycling industries.

[0042] As implemented, the blocking layer comprising thermoplastic materials, iron oxides and, if applicable, the protective layer of liquefied plastics materials will provide supplementary protection to radioactive packages to counter their degradation over time, in particular by water, and will resist any radiation.

[0043] The protective layer is preferably applied by dipping the radioactive package into a bath of liquefied polymers, after which the radioactive package is dried so as to obtain a protective layer of a thickness of 2-3 mm.

[0044] The thermoplastic raw material will preferably be obtained by collection or recovery in waste sorting facilities or sanitary landfill sites. It comprises for example computer or telephone casings, or any other largely unidentified plastics casing. This kind of thermoplastic material is not considered by the recycling industry and is unwelcome in sanitary landfill sites because it is not

biodegradable. It is mainly PS/ PE/ PP/ PVC/ ABS or mixtures thereof of any origin.

[0045] It should be noted that this fraction often contains little or no PS since PS is normally collected separately. It should, however, be noted that any PS which may be present will be micronised and will be at least partially solubilised during manufacture of the blocking layer or during manufacture of the protective layer.

[0046] In order to obtain this blocking layer, one or more thermoplastic polymers, preferably PS (polystyrene), preferably originating from recycling facilities, are liquefied with the assistance of a solvent, preferably a mixture of acetone and pinene, at ambient temperature and, on the one hand, micronised particles of thermoplastic materials, preferably obtained by collection or recovery in the waste sorting facilities or sanitary landfill sites described above, and, on the other hand, micronised iron oxide particles. This mixture may be obtained by any conventional means.

[0047] The advantage of using micronised particles resides in their roughness and the consequent large specific surface area. This surface appearance allows the particles to be effectively bound in the polymer matrix based on liquefied PS.

[0048] The blocking layer therefore comprises, on the one hand, particles of iron oxides, particles of thermoplastic material and a matrix based on liquefied and resolidified thermoplastic materials, preferably on polystyrene.

[0049] The viscosity of the mixture is adjusted such that it is suitable for application onto the radioactive package by a spraying method, preferably by a method of the airless spraying type.

[0050] Once applied onto the radioactive package, the solvents evaporate and the liquefied part solidifies and forms the blocking layer comprising a thermoplastic polymer matrix in which the particles of thermoplastic material and iron oxides are bound. This blocking layer makes the packages insensitive to weather conditions and makes it possible to store them for very long periods

without requiring repackaging. At the same time, it also enables a reduction in the radioactivity emitted by the package.

[0051] It is important to emphasise that, unlike the materials described in international patent application WO00/02855 or patent application EP0055671, no polymerisation reaction occurs between the various components of the blocking layer as described in the present patent application. Furthermore, the materials described in the cited prior art contain little or no iron oxide.

[0052] According to another preferred embodiment, the blocking layer may also be used to secure sludges arising from the separation of spent fuel from plutonium\* and uranium\* (which are recycled\*). These sludges are directly mixed into a liquefied mixture of thermoplastic materials and particles of thermoplastic polymers micronised to 500 microns, and an iron oxide powder micronised to between 80 and 250 microns, in a sufficient quantity to make them homogeneous and easier to manage.

[0053] Once such homogeneity has visibly been achieved, this composition will be coated with a pasty or even liquid polymeric blocking layer which will impart long-term resistance thereto (degradation by water and migration of radionuclides into the geosphere), before being cast in stainless steel drums.

[0054] According to still another preferred embodiment, the method may also be used to secure concrete serving to isolate waste from power station dismantling (metal cladding, gloves, overboots, tools, resin filters etc.). To this end, between 50 and 120 kg/m<sup>3</sup> of a matrix based on liquefied thermoplastic materials comprising a mixture of thermoplastic materials micronised to between 400 and 700 microns, and an iron oxide powder micronised to between 80 and 250 microns, is mixed with the other ingredients of the concrete.

[0055] Incorporating the mixture will prevent water from penetrating inside the structure and causing internal changes of various kinds, or the degradation of cement-based packages.

[0056] According to still another embodiment, it is also possible to apply a blocking layer onto radioactively contaminated surfaces, e.g. in nuclear power stations or repackaging facilities or indeed in laboratories. Application of the blocking layer makes it possible to secure the environment and will allow decontamination to be carried out under better secured conditions.

### **Brief description of the drawings**

[0057] Other distinctive features and characteristics of the invention will be revealed by the detailed description of some advantageous embodiments given below by way of example, with reference to the appended drawings, in which:

Figure 1 is a cross-section of a radioactive package,

Figure 2 is a reproduction of the absorption surface of the polymer micronised to between 400 and 700 microns under an electron microscope.

Figure 3 is a schematic diagram showing one operating mode of the method.

[0058] Figure 1 shows a radioactive package protected by a glass matrix 10 covered with a blocking layer 20 comprising a matrix based on liquefied thermoplastic materials comprising a mixture of plastics materials micronised to 500 microns, and an iron oxide powder micronised to between 80 and 250 microns, applied uniformly onto said vitrified matrix with the assistance of airless spraying equipment.

[0059] A second layer, a protective layer 30, of liquefied plastics materials is applied onto the blocking layer according to the previously liquefied polymer method and then dried.

[0060] In order to obtain this protective layer 30, the package previously coated with the blocking layer is dipped into a bath of polymers previously liquefied with the assistance of environmentally acceptable reagents (acetone-pinene mixture) which are non-hazardous to humans and the environment. These polymers in paste form, given the low-temperature processing of the reagents, will be heated up to 160°C in a heated tank in order to solubilise the plastics completely. During this operation, the vapours from the reactants used are

condensed in a cold trap by exploiting the boiling point of the reagents used. The radioactive package is then removed from the bath and, after drying, this polymer layer will secure the package against deterioration by water. In this way, any dispersion of radioactive substances into the environment resulting in a risk of uptake by living organisms is avoided.

[0061] Figure 2 shows the absorption surfaces of open cavities 50 of the mixture of polymers micronised to between 400 and 700 microns under an electron microscope. The solid outlines 60 of these cavities are hatched, so revealing the huge absorption surface of these polymers.

[0062] Figure 3 is a schematic diagram of the course of the various steps in the method carried out industrially:

- recovery of the polymers in a waste sorting facility, or elsewhere (a).
- transfer to a microniser (b).
- forwarding to the solubilising tank with a heated wall system (c)
- radioactive package vitrified by the glass matrix (d).
- application of the first layer of liquefied polymers mixed with iron oxides having the capacity of a binder onto the glass matrix using an airless spraying system (e).
- application of the second 2 to 3 mm layer of previously micronised liquid polymers resulting in a chemical coating which will protect the package from attack by water (f).
- transfer of the packages secured by the method to a storage site (g).