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Abstract

The sealing jointing compounds applied in practice and already examined for decontaminability will be presented here.

Solvent-free sealing compounds, emulsifiable in water, with low molecular epoxy resins as binders, quite a number of curing versions, and little hygroscopic filler mixtures adapted in grain size have been tested with a view to ceramic tile jointing in nuclear facilities. The sealing compounds were examined before and after exposure to gamma irradiation (300 KGy energy dose) for decontaminability, color, gloss and resistance to decontaminants. Out of fourteen compounds exhaustively investigated ten are very well decontaminable and four well decontaminable. After exposure to radiation no or only minor changes in color and gloss, respectively, were observed. Visible changes such as cracking, bubbles, etc. were not found and the resistance to decontaminants was neither affected.

It has even been possible to replace in the well decontaminable sealing compounds developed until now part of the epoxy resin binder with elasticizing components such as Thiokol which is very important as a base material for sealing compounds in the construction industry, but difficult to decontaminate.

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Kurzfassung

Es werden die bisher auf Dekontaminierbarkeit geprüften in der Praxis verwendeten Fugendichtungsmassen vorgestellt.

Für die Verfugung von keramischen Fliesen in kerntechnischen Anlagen wurden wasseremulgierbare und lösemittelfreie Dichtungsmassen auf der Bindemittelbasis niedermolekularer Epoxidharze, verschiedenen Aushärtungsvarianten und in der Korngröße abgestimmten inerter Füllstoffmischungen getestet.Sie wurden vor und nach der Gammabestrahlung (Energiedosis 300KGy) auf Dekontaminierbarkeit, Farbe, Glanz und Dekontaminationsmittelbeständigkeit geprüft. Von 14 abschließend untersuchten Systemen waren 10 sehr gut und 4 gut dekontaminierbar. Nach der Strahlenbelastung kam es zu keiner oder nur sehr geringen Farb- bzw. Glanzänderung. Sichtbare Veränderungen wie Rißbildung, Blasen etc. wurden nicht festgestellt, und die Dekontaminationsmittelbeständigkeit war auch nicht beeinträchtigt.

In den entwickelten sehr gut dekontaminierbaren Dichtungsmassen konnte sogar ein Teil des Bindemittels Epoxidharz durch elastifizierende Komponeten z.B. Thiokol, das im Bauwesen als Grundstoff für Dichtungsmassen große Bedeutung hat aber schwer zu dekontamieren ist, ersetzt werden.

Contents

1. Introduction and Problem

In nuclear facilities and radiochemical laboratories contamination of the walls and especially of the floors can hardly be avoided because radioactive materials are handled there. As soon as the admissible limits according to the Radiation Protection Ordinance, laid down in Annex IX of 30 June, 1989, are exceeded, the contamination must be removed immediately and, if possible, without damage to the surface.

Therefore, poorly decontaminable concrete surfaces inclusive of the joint fillers must be coated with well decontaminable coating materials and jointed with well decontaminable sealing jointing compounds so as to allow contaminations to be removed perfectly and quickly.

Liquid tight covering joints are provided on walls and on floors using elastic sealing compounds, whereas for floor and wall tiles less elastic sealing compounds are used. Jointing of floor coverings (PVC floors without, rubber floors with joints) is achieved by welding. A great variety of requirements, which follow from other impacts such as the action of chemicals, radioactive radiation, or from aspects of building physics, must be taken into account.

Joints, pores or cracks which have developed due to improper material used or poor workmanship, may cause difficulties in decontaminating these surfaces or their being non-decontaminable. Removal of such contaminations calls for much expenditure in terms of time and costs. Taking into account special protective measures, the parts contaminated by radioactivity must be removed. The wastes arising have to be treated as radioactive wastes. They have to be packaged and transferred into a storage facility licensed for this purpose which requires a great deal of expenditure.

Since the early days of nuclear engineering, industry has been concerned with fabricating suitable surface materials and today it is capable of offering a variety of products which largely meet the requirements. The results of well decontaminable wall and floor coatings, floor coverings and non-metallic materials have already been published [1,2,3].

This is a report about the sealing compounds already examined for their decontaminability at the Karlsruhe Nuclear Research Center and proven in practical application. Moreover, results of decontamination experiments performed on less elastic sealing compounds (based on epoxy resins used to joint floor and wall tiles (plates)) prior to and after radiation exposure will be presented.

2. Results of Decontamination of Sealing Compounds Proven in Practical Application

The sealing compounds examined for their decontaminability until mid-1990 have been entered in Table 1. These are curing and in the first line elastic sealing compounds.

A typical representative of the curing products is linseed oil putty which has been used quite a long time to fix glass panes. The sealing compound which nearly turns into cement expands little, is unsuited for concrete jointing and not recommendable for use in areas susceptible to contamination.

According to the present status of development elastic sealing compounds are used in practical application for proper sealing of movable joints [4,5].

Sprayable viscous one- or two-component material is transferred into the more or less elastic condition by physical drying or chemical crosslinking.

One-component sealing compounds need the humidity of the air to be able to activate the crosslinking agent in the system. Crosslinking proceeds slowly because the humidity must diffuse through the already polymerized external layer. Two-component sealing compounds react only perfectly if the two components have been very well mixed. At elevated temperature they react clearly faster than at low temperature. Low temperatures may even prevent the chemical reaction from taking place.

Silicone sealing compounds: In practice, two crosslinking systems have been widely applied, namely the acid (acetic acid) system and the alkaline (amines) system. Good adhesion is achieved when alkaline crosslinking compounds are used on alkaline carriers and acid crosslinking compounds on acid carriers. The elasticity properties of the silicone sealing compounds are maintained practically unchanged over a very large range of temperatures (-50°C to +200°C). They are characterized by good resistance to aging, radiation, chemicals and weathering and are very well decontaminable. Drawback: They cannot be brushed over.

Polysulfide sealing compounds: As they cure fast, the joints can be subjected to stress after a short while. They excel by good elasticity in the temperature range between -50°C to +90°C and by resistance to chemicals and weathering. The poor decontaminability can be compensated by brushing over with well decontaminable elastic coatings.

Polyurethane sealing compounds are characterized by good resistance to chemicals and weathering. They are quite well decontaminable. Not all the polyurethane sealing compounds can be brushed over.

Epoxide sealing compounds are characterized by very good resistance to chemicals and radiation. They can be brushed over and are very well decontaminable although little elastic.

3. Epoxy Resin Base Sealing Compounds Used to Joint Ceramic Tiles

In nuclear facilities ceramic tiles are used in special applications such as basin lining, acid handling rooms, washing facilities, laboratories, etc. Normally, low elasticity epoxy resin base sealing compounds are used in jointing which, however, exhibit excellent resistance to the attack by chemicals and are very well decontaminable.

In those rooms the jointed tiles are subjected to more or less harsh conditions because they are alternately exposed to wetting, dryout and changes in temperature.

Not only the tiles and sealing compounds must be well decontaminable but, in addition, jointings must be made non-porous and liquid tight with greatest care so that the removal of contaminations is not made more difficult or even made impossible.

Therefore, only large tiles should be laid on surfaces where there is a risk of contamination because with large tiles the number of joints is relatively small and there is more guarantee that the surfaces are free of pores and cracks - obviously on the assumption of good workmanship.

3.1 Composition and Application

A two-component epoxide material was used in irradiation and decontamination experiments which has proved valuable for many years in making well decontaminable joints. Some of the low molecular epoxy resins, which were free of solvents and emulsifiable in water, respectively, were combined with hydrocarbon resins or polysulfide, various curing agents and varying amounts of fillers and pigments in order to be able to find out the influence exerted by these products on the radiation tolerance and decontaminability (Table 2).

Steel sheets, 50 mm x 50 mm x 1 mm in size, were coated on both sides with the sealing compounds and cured under normal climatic conditions.

3.2 Stress Experienced by the Sealing Compounds as a Result of Gamma Radiation

After curing of four weeks duration under normal climatic conditions, accompanied by ventilation, the coated specimens were irradiated with the Gammaster company, Munich, in conformity with the German standard DIN 53781 (revised version in preparation). The distance of the Co-60 radiation source from the specimens was selected such that the energy dose rate was 900 to 100 Gy/h (Table 3).

3.3 Evaluation of the Sealing Compounds after Gamma Irradiation

3.3.1 Visible Changes on the Surface

The evaluation was made by visual inspection and comparison with the non-stressed specimens.

The measure of evaluation for visual comparison was the relative grading scale according to DIN 53230.

Identifying Number	Meaning
0	no changes
1	minimal changes
2	little changes
3	moderate changes
4	strong changes
5	very strong changes

For all specimens the color and luster do not undergo any changes or only little changes after radiation exposure to 300 KGy (0.3 MGy) (identifying numbers 0 to 1). Other changes such as bubble or crack formation, crinkling, chalking or swelling have not been observed.

3.3.2 Resistance to Decontaminating Solutions

In order to be able to assess any changes due to decontaminating solutions ethanol, 10% aqueous Papan-Dekopan and Senzacon-acid-solutions were applied to the surfaces to be tested. Even after 24 hours of reaction the irradiated as well as the unirradiated specimen surfaces did not exhibit any changes or just minor changes (identifying numbers 0 to 1).

3.4 Results of Decontamination

Sealing compounds contain high portions of different filler materials. The combination of fillers and their amount influence in different ways major technical properties as well as the decontaminability of the sealing compounds. Favorable influences are e.g. the extension with increasing temperature, the behavior during fires, the reduction in susceptibility to damage of the pores. On the other hand, more water taken up by the sealing compounds produces mainly negative results on decontaminability. This holds true above all when fillers and pigments are hygroscopic. In that case, the radionuclides adhere to these particles.

Therefore, it had to be determined in advance which of the little hygroscopic filler mixtures are suited as sealing compounds with a view to achieving good decontaminability.

The decontamination tests were performed in conformity with DIN 25415, Pt. 1/ISO 8690. Different from the said standards, only two and three specimens, respectively, were tested for each radionuclide instead of five.

3.4.1 Results in the Absence of Preirradiation

In Table 4 the results have been compiled of the decontamination tests of sealing compounds consisting of low molecular epoxy resin binders (systems 1 through 14).

Very well decontaminable binders are:

- polyamine cured sealing compounds emulsifiable in water, even with increased filler fractions, but without excessive amounts of emulgating or diluting agents added;
- solvent-free sealing compounds (except for system 9);
- solvent-free sealing compounds with some of the epoxy resin replaced with Thiokol or hydrocarbon resins.

3.4.2 Results after Gamma Irradiation with 300 KGy

It appears from Table 4 that the results of decontamination for systems containing epoxy resins after gamma irradiation are at the same grading level as the results obtained prior to irradiation.

For the systems 11 through 13 gamma irradiation probably intensifies crosslinking of the binder and the curing agent. The specimens with lower residual count rates compared to the unirradiated ones show a minor improvement of decontaminability.

4. Summary

Of the more than 40 sealing compounds tested since 1960 products with epoxy resin, polyurethane and silicone as binders are suited for jointings in nuclear facilities because very good decontaminability constitutes an indispensable prerequisite. By contrast, sealing compounds with Thiokol as the binder can be used with reservations only and linseed oil putty cannot be used at all.

The binder base recommended for the production of decontaminable sealing compounds used to joint ceramic floor and wall tiles is low molecular epoxy resin. For products emulsifiable in water modified polyamines and for solvent-free compounds aliphatic, cycloaliphatic polyamine adducts with Mannich base as curing components furnished the best values. The results show that the decontaminability is very good also in case of high contents of e.g. aluminium silicates, quartz mixtures, heavy spar (baryte) as fillers.

It was even possible to replace part of the epoxy resin binder with hydrocarbon resins or Thiokol without deteriorating the decontaminability.

Use of Thiokol is of great importance because these polysulfide sealing compounds are most frequently used in Germany. But sealing compounds based exclusively on Thiokol cannot be used in all cases where contaminations may occur because they are only inadequately decontaminable.

Of a total of fourteen epoxy resins containing systems exhaustively examined ten are **very well** and four are **well** decontaminable. All systems examined after exposure to gamma irradiation do not undergo changes or only minor changes in color and/or luster. The same holds true for the resistance to decontaminating solutions.

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Table 1 Results of Decontamination of Sealing Compounds

Sealing Compounds	Use as One- and/or Two-component Compounds	Grades for Decontaminability			
		Very good	Good	Moderate	Poor
<u>Curing</u>					
Linseed oil putty	one-, rarely two-component compound	-	-	2	1
<u>Elastic</u>					
Polysiloxanes (silicone)	one-component compound	7	3	3	2
Polysulfides (Thiokol)	one- and two-component compounds	-	2	3	5
Polyurethanes	one- and two-component compounds	1	2	1	2
<u>Less elastic</u>					
Epoxides	two-component compound	2	1	2	2

Table 2 Composition of the Sealing Compounds

System	Shade of Color	Curing Agent, Additives	Fillers 1)	Solids wt.%
Low Molecular Epoxy Resin Base Sealing Compounds Emulsifiable in Water				
1	grey	modified polyamine	heavy spar	95
2	grey	modified polyamine elevated filler content	heavy spar	96
3	grey	modified polyamine diluting agent	heavy spar	95
4	grey	modified polyamine emulgator	heavy spar	95
5	grey	modified polyamidoamine elevated filler content	heavy spar	100
6	grey	modified polyamine	heavy spar + quartz mixture	97
Low Molecular Epoxy Resin Base Solvent-free Sealing Compounds				
7	grey	cycloaliph. polyamine adduct	heavy spar	100
8	grey	aliph. + cycloaliph. amines	quartz mixtures	100
9	grey	aliph. diamine	quartz mixtures	100
10	grey	aliph. diamine + Mannich base	quartz mixtures	100
Flexible Low Molecular Epoxy Resin Base Solvent-free Sealing Compounds				
11	light beige	modified cycloaliph. amines	aluminium silicate + baryte	100
12	light beige	modified cycloaliph. amines + solvent	aluminium silicate + baryte	97
Solvent-free Sealing Compounds with Binder Mixtures as the Base				
13	light beige	epoxide + Thiokol	aluminium silicate + baryte	100
14	light beige	expoxide + hydrocarbon resin	aluminium silicate + baryte	100

1) In all systems with titanium dioxide (rutile) and suitable color pigments added

Table 3: Gamma Irradiation of Sealing Compounds

(irradiation in exposure room at Gammaster company, Munich)

Radiation Source	Co-60
Mean quantum energy	1.17/ 1.33 MeV
Homogeneity of the radiation field	± 10 %
Mean energy dose rate 1)	900 - 1000 Gy / h
Energy dose	300 K Gy
Energy dose measurement	red-acrylic and alanine
Exposure room	150 m^3
Specimen size	50 mm x 50 mm x 1-5 mm
Ambient atmosphere	air, rel. humidity 30 to 70 %
Ozone content during exposure	≈ 0.5 ppm
Specimen temperature during exposure	15 to 25° C
Ventilation during exposure	continuous, about 10,000 m^3 / h

1) in this specific case

Tab.4 Results of Decontamination of Sealing Compounds prior to and after Gamma-Irradiation

System	Curing Agents, Additives	Results of Decontamination according to DIN/ISO 25415, Pt. 1					
		Prior to Irradiation			After Irradiation,300 KGy		
		Co-60 cpm	Cs-137 cpm	Co/Cs-Residual Count Rate cpm	Co-60 cpm	Cs-137 cpm	Co/Cs-Residual Count Rate cpm
1	modified polyamine	2850	3110	2980 very good	3420	2080	2750 very good
2	modified polyamine elevated filler content	3400	2200	2800 very good	2920	2400	2660 very good
3	modified polyamine diluting agent	4300	4170	4235 good	2530	6420	4475 good
4	modified polyamine emulgator	5550	4850	5200 good	4400	10500	7450 good
5	modif. polyamidoamine elevated filler content	11640	7420	9530 good	9200	8260	8730 good
6	modified polyamine	590	1810	1200 very good	780	1560	1170 very good
7	cycloaliph. polyamine additive	1420	2040	1730 very good	2100	980	1540 very good
8	aliph. + cycloaliph.amines	930	1090	1010 very good	720	1780	1250 very good
9	aliphatic diamine	5900	4900	5400 good	5200	4720	4960 good
10	aliph. diamine + Mannich-base	900	760	830 very good	750	1510	1130 very good
11	modified cycloaliphatic amines	3700	2000	2850 very good	2300	2200	2250 very good
12	modif. cycloaliph. amines + solvent	3600	2220	2910 very good	2140	2460	2300 very good
13	epoxide + Thiokol	3600	2220	2910 very good	2140	2020	2080 very good
14	epoxide + hydrocarbon resin	3420	2100	2760 very good	2400	2800	2600 very good