Materials for the manufacture of transport containers

The invention relates to the use of polyethylene materials for the manufacture of massive transport and storage containers and also for the manufacture of lined transport and storage containers for chemicals, especially for the transport and storage of high-purity liquid chemicals for the electronics industry. The invention further relates to the use of these materials for the manufacture of the equipment required to discharge the chemicals from the transport containers and to fill said containers.

In many instances the manufacture of electronic components requires liquid chemicals which are subject to the strictest purity standards. This is particularly the case for the manufacture of large-scale integrated microchips. On the one hand, the purity of these chemicals is at a level where it is not sufficient just to manufacture the chemicals to the purity demanded; it is also necessary to ensure that no further impurities enter the product during shipping or during storage and handling. On the other hand, the storage and transport safety must be guaranteed because the aggressive properties of some of these chemicals makes them difficult to handle and store. In many cases they are also toxicologically harmful or have hazardous chemical properties. An accidental spillage, e.g. due to damage to the transport container or leaks, caused by the aggressive properties of some of these chemicals, must be ruled out with a high degree of certainty.

Because of the demands on the chemicals to be shipped, the choice of material for such transport containers must be governed primarily by the exclusion of any impurities. This demand is normally satisfied by containers made of fluorinated or perfluorinated materials or containers lined with such materials.

According to demands, these transport and storage containers are manufactured as the pressureless version or as pressure containers.

Pressureless containers must not be exposed to any internal pressure applied from outside.

Similarly, the liquid chemicals must be discharged from such containers without the application of pressure, i.e. with the aid of pumps. These pumps necessarily have moving parts, so the possibility of impurities due to wear occurring in the region of the pumps cannot be completely ruled out.

However, especially where pressure resistant containers are used, it is known to discharge chemicals by introducing pressurized inert gases through dip tubes so that no pumps are required and no wear can thus occur. DE 36 36 886 has disclosed a transport container for high-purity liquid chemicals which has a double-shell inner container, the innermost lining of which consists of a fluorinated plastic. The multi-shell design of this transport container is such that it can be pressurized. The disadvantages, however, are on the one hand that the only materials suitable for the manufacture of such inner linings are special fluorinated plastics which have to be produced in elaborate and therefore expensive processes, and on the other hand that the processability of these plastics is made more difficult by the fact that, because of the high purity demands on the chemicals to be shipped, not just any processing aids can be added to the plastic and contamination by tools and environmental factors has to be extensively minimized.

As regards the choice of material for the manufacture of massive transport containers, the polymer material must have not only resistance to possible leaching and embrittlement by chemicals to be shipped, but also an adequate rigidity as well as a degree of elasticity, so that containers made of the material are insensitive and stable to pressure and impact and do not tend to deform or crack. Furthermore, these material properties must be durable so that, even during prolonged storage, both the purity of the chemicals to be shipped and the properties of the container are preserved.

One object of the invention is therefore to

provide a suitable material for the manufacture of transport containers for high-purity liquid chemicals, and the associated equipment, which is economic to produce, is obtained in high purity during synthesis, contains only a very low concentration of polymerization catalysts, if any, and can be processed easily, if possible without the addition of processing aids or with the addition only of processing aids which do not have a detrimental effect in use or which are not leached out of the material by the chemicals to be shipped. Another object of the invention is to provide a suitable polymer material from which it is possible to manufacture both massive storage and transport containers for high-purity liquid chemicals, and linings for corresponding containers which can be pressurized.

The object is achieved according to the invention by the use of HD polyethylene (HD = high density) for the manufacture of massive storage and transport containers for high-purity liquid chemicals for the electronics industry, and the associated equipment, and for the manufacture of linings for corresponding containers which can be pressurized, and the associated equipment. The object is achieved in particular by the use of HD polyethylene with a specific density of 0.940 - 0.970 g/cm^3, especially 0.942 - 0.961 g/cm^3.

According to current opinion, the only suitable materials for containers which are to be used for shipping high-purity acids or bases are plastics based on fluorinated hydrocarbons. Examples of such materials are polytetrafluoroethylene (PTFE), perfluoroalkoxy polymers (PFA), polyvinylidene fluorides (PVDF) or poly(ethylene/chlorotrifluoroethylene) (ECTFE), which are described in general usage by the well-known trademark "Teflon". For those skilled in the art, plastics described as Teflon are insensitive to the effect of aggressive chemicals such as particularly strong acids or bases, and also to the effects of temperature. These plastics are expensive and therefore uneconomic materials.

Experiments have now shown, surprisingly, that non-fluorinated plastics can also be used for the manufacture of high-quality transport containers and the associated equipment, e.g. dip tubes, pump parts and hoses, for high-purity liquid chemicals for the electronics industry. Selected HD polyethylenes (high density polyethylenes), namely polyethylenes with a specific density in the range 0.940 - 0.970 g/cm^3, especially 0.942 - 0.961 g/cm^3, have proved to be particularly suitable materials for the desired use. Furthermore, these polyethylene grades are distinguished analytically by a particularly low content of catalyst residues. Therefore, compared with other materials, these materials release particularly small amounts of ionic impurities when in contact with both basic and acidic high-purity chemicals. Also, when in contact with chemicals, comparatively few particles are produced due to interactions between the chemicals and the material. This is particularly important with regard to use of the material in the manufacture of the equipment for filling the containers and discharging the chemicals. Surprisingly, these materials are suitable both for the manufacture of dip tubes and for the manufacture of pumps which are required for discharging the high-purity chemicals from pressureless transport containers and conveying them to the processing site.

This was particularly surprising because other corresponding polyethylene materials which for many years have been used successfully for the transport of hazardous goods are suitable as unsuitable for the transport and storage of high-purity liquid chemicals. When tested, these plastics were found to release too many particles and an unacceptable amount of ionic impurities.

Polyethylene materials marketed by BASF under the trademark Lupolen have proved to be particularly suitable materials for said purpose. In storage tests, the material grades commercially available under the names Lupolen 6021 D, Lupolen 5021 D, Lupolen 4261 A Q 149 and Lupolen 4261 A Q 135 have proved to be particularly

suitable from this group of polyethylene specifications.

These materials are particularly suitable for the use according to the invention because they are extrudable but can also be welded without a loss of quality. This affords the possibility of manufacturing almost any size of container by welding appropriate slabs of this material. By means of textile fabric applied to one side of these slabs and anchored in the material, it is possible to prefabricate relatively thin-walled inner containers. By the application of glass fibre-reinforced polyester resin, it is possible to manufacture containers which are stable per se and which, when designed appropriately, comply with the regulations governing pressure containers. Structurally these containers consequently have a double-shell design. In particular, said structure comprises shells which are joined together, the inner shell consisting of the HD polyethylene selected according to the invention and the outer shell consisting of a glass fibre-reinforced polyester resin. There is the further possibility of modifying the surface of the manufactured containers by methods known to those skilled in the art, for example by painting, backing or dispersion coating with suitable barrier polymers or by covering with thin metal foil. Barrier polymers suitable for this purpose are polyamide, polyester, polyvinylidene difluoride or polymers based on acrylonitrile. The permeability to gases, vapours and liquids can be reduced in this way.

The values given in the following Tables will explain the invention in greater detail but are not intended to limit the invention to said Lupolen polyethylene materials studied.

Table 1

Release of cationic impurities from polyethylene materials in the presence of high-purity chemicals

Values found in ng/g pellet	Lupolen 5021 D 1st elution Time: 7 days Chemical: HCl 35% 40 °C	Lupolen 6031 M 1st elution Time: 7 days Chemical: HCl 35% 40 °C	Lupolen 6060 D 1st elution Time: 7 days Chemical: HCl 35% 40 °C	LLDPE Neste NCPE 8682 1st elution Time: 7 days Chemical: HF 49% 40 °C	LLDPE Neste NCPE 8682 2nd elution Time: 7 days Chemical: HF 49% 40 °C	VEPE Scair-link 8000 G 5 1st elution Time: 7 days Chemical: HF 49% 40 °C
Aluminimum	16	170	8	218	238	815
Antimony	-	-	-	-	-	-
Arsenic	-	-	-	-	-	-
Barium	-	-	-	3	-	3
Beryllium	-	-	-	-	-	-
Bismuth	-	-	-	72	84	18
Boron	-	-	-	-	-	-
Cadmium	-	-		-	-	-
Calcium	6.6	60	17	97	110	147
Chromium	4	0.3	45	-	-	-
Cobalt	-	-	-	-	-	-
Copper	-	-	-	-	-	-
Gallium	-	-	-	-	-	-
Germanium	-	-	-	-	-	-
Gold	-	-	-	-	-	-
Indium	-	-	-	-	-	-
Iron	18	24	13	52	17	86
Lead	-	-	-	-	-	-
Lithium	-	-	-	-	-	-
Magnesium	1.5	39	-	62	38	82
Manganese	-	-	-	-	-	-
Molybdenum	-	-	-	-	-	-
Nickel	-	-	-	-	-	-
Platinum	-	-	-	-	-	-
Potassium	3	-	-	30	45	94
Silicon	-	-	-	-	-	-
Silver	-	-	-	-	-	-
Sodium	20	-	16	110	150	300
Strontium	-	-	-	-	-	-
Thallium	-	-	-	-	-	-
Tin	-	-	-	-	-	1.5
Titanium	-	30	-	86	5	16
Vanadium	-	-	-	-	-	3
Zinc	0.9	3.6	8	4800	714	72
Zirconium	-	-	-	-	-	-

Table 2

Release of cationic impurities from other polyethylene materials in the presence of high-purity chemicals

Values found in ng/g pellet	Hostalen GM6255 1st elution Time: 6 days Chemical: HF 49% 25 °C	Hostalen GM6255 1st elution Time: 26 days Chemical: HF 49% 25 °C	Lupolen 4261A Q135 1st elution Time: 7 days Chemical: HCl 35% 40 °C	Lupolen 5261Z Q135 1st elution Time: 7 days Chemical: HCl 35% 40 °C	Lupolen 5261Z Q445 1st elution Time: 7 days Chemical: HCl 35% 40 °C	Lupolen 6021 D 1st elution Time: 7 days Chemical: HCl 35% 40 °C
Aluminimum	60	0.5	60	1040	110	17
Antimony	-	-	-	-	-	-
Arsenic	-	-	-	-	-	
Barium	1.5	-	-	-	-	-
Beryllium	-	-	-	-	-	-
Bismuth	-	-	-	-	84	-
Boron	-	-	-	-	-	-
Cadmium	-	-		-	-	-
Calcium	90	0.8	10	33	45	3.6
Chromium	13	1.3	70	110	147	3.6
Cobalt	-	-	-	-	-	-
Copper	4	-	1.5	-	-	-
Gallium	-	-	-	-	-	-
Germanium	-	-	-	-	-	-
Gold	-	-	-	-	-	-
Indium	-	-	-	-	-	-
Iron	80	2	63	33	33	6.3
Lead	0.5	-	-	-	-	-
Lithium	-	-	-	-	-	-
Magnesium	26	-	1.5	3	4.5	-
Manganese	1.3	-	0.3	-	-	-
Molybdenum	-	-	-	-	-	-
Nickel	2	-	1.5	-	-	-
Platinum	-	-	-	-	-	-
Potassium	10	-	30	2	1.5	6.3
Silicon	-	-	-	-	-	-
Silver	-	-	-	-	-	-
Sodium	7	-	16	36	24	24
Strontium	-	-	-	-	-	-
Thallium	-	-	-	-	-	-
Tin	-	-	-	-	-	-
Titanium	-	5	2.5	-	-	-
Vanadium	-	-	-	-	-	-
Zinc	29	-	1.5	0.3	2.4	-
Zirconium	-	-	-	-	-	-

THIS SHEET HAS BEEN REPLACED

PATENT CLAIMS

1. Use of HD polyethylene (HD = high density) for the manufacture of massive storage and transport containers for high-purity liquid chemicals for the electronics industry.

2. Use of HD polyethylene for the manufacture of linings of storage and transport containers for high-purity liquid chemicals for the electronics industry.

3. Use of HD polyethylene for the manufacture of the equipment, especially dip tubes, and liquid-conveying pumps for storage and transport containers for high-purity liquid chemicals for the electronics industry.

4. Use according to Claims 1 to 3, characterized in that the polyethylene has a specific density of 0.945 - 0.970 g/cm^3.

5. Use according to Claim 2, characterized in that the lining of the storage and transport container is a two-shell inner container whose inner shell is made of an HD polyethylene and surrounded by a glass fibre-reinforced outer shell.

6. Use according to Claims 1 - 5, characterized in that the HD polyethylene is from the group comprising Lupolen 6021 D, Lupolen 5021 D, Lupolen 4261 A Q 149 and Lupolen 4261 A Q 135.

7. Storage and transport containers for high-purity liquid chemicals for the electronics industry, made of HD polyethylene.

8. Linings for storage and transport containers for high-purity liquid chemicals for the electronics industry, made of HD polyethylene.

9. Dip tubes for use in storage and transport containers for high-purity liquid chemicals for the electronics industry, made of HD polyethylene.

10. Liquid-conveying pumps for high-purity liquid chemicals for the electronics industry, made of HD polyethylene.

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