Research progress of water-based release agents

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Abstract. A mould release agent is an additive that makes the moulded product easy to detach from the mould, it forms a protective film on the product to ensure the surface quality of the mould. Mold release agents are divided into water-based release agents, oil-based release agents and powder-based release agents. Water-based release agents are widely used because they have the advantages of low price, good release effect, green environment protection, smooth casting surface, good air tightness and good automaticity operation.

According to the effective release material in the mold, release agent can be divided into silicone oil type, wax and fatty acid type water-based mold release agent. In this paper, the composition, properties and application characteristics of various water-based release agents were analyzed, and the future development direction of water-based release agents was forecasted.

Keyword: Release agent; water - based release agent; silicone oil release agent.

1. Introduction

A release agent is an additive that allows the moulded product to be easily separated from the mould, forming a protective barrier film on the product and ensuring the surface quality of the mould. The principle is that the release agent forms a special insulating film which reduces the adsorption of the product to the mould. This insulating film is only micron thick and highly heat resistant and is a chemically connected film, the main function of which is to reduce the peeling force so that the moulded part can be easily separated intact within a certain temperature range[1-6]. China is a large producer and consumer of plastics and rubber industry, since 2010, the annual production of plastics and rubber has exceeded 60 million tons, the annual production and consumption capacity are ranked first in the world, with the rise of the rubber and plastic industry, the amount of mold release agent is also increasing year by year, so the market size is huge. Mould release agents are widely used in moulded products of elastomers such as rubber and plastics. The specific performance requirements of the release agent are as follows: good release, good continuity of release and the formation of a homogeneous film even for complex shaped moulded objects. Good formability and superior secondary processability: when the release agent is transferred to the formed object, it has no adverse effect on the processed object such as plating, hot press moulding, printing, finishing and bonding. Easy coating, heat resistance and good pollution resistance. Good stability, good physical and chemical stability when used with the compound. Low flammability, low odor, low toxicity and high production efficiency[7-11].

Water-based release agents are widely used due to their excellent price, good release effect, green environment protection, smooth casting surface, good air tightness and good automaticity operation[12-16]. After spraying, it is able to produce a thin layer of only micron thickness on the surface of the mould, which not only reduces the impact of the metal liquid on the cavity during pressing and forming, but also reduces the wear of the casting and the cavity, ultimately protecting the cavity and acting as a lubricant. At the same time, it can also adjust the temperature of each part of the mould, so that the internal temperature of the mould remains balanced, thus improving the service life of the mould, therefore, water-based mold release agent instead of oil-based mold release agent has become an inevitable trend. At the same time, it is able to adjust the temperature of each part of the mould, so that the internal temperature of the mould remains balanced, thus increasing the service life of the mould. Therefore, it has become an inevitable trend for water-based release agents to replace oil-based release agents[17]. Depending on the nature of the release agent, mold release agents can be divided into water-based release agents, oil-based release agents and powder-based release agents. Compared to oil-based release agents, water-based release agents are safe, clean, non-polluting, do not damage the surface of the casting, are easy to cool and produce fewer internal pores, and are increasingly used. Water-based release agents have the advantage of

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being less expensive and less costly than powder release agents [18]. Water-based release agents can be classified as silicone, wax or fatty acid based on the effective release substance in the release agent.

2. Silicone oil-based release agents

The term silicone oil is usually used to refer to dimethicone oil [19]. Silicone oils have a lower surface tension than typical organic oils and solvents, are oxidatively stable, chemically inactive and have no physiological activity. Therefore, silicone oil mold release agent has the characteristics of easy to release, does not pollute and corrode the mold and product, use low concentration, can be used in the coating many times, non-toxic, and therefore is widely used in rubber, packaging, plastic synthesis, glass manufacturing, printing production, precision casting and other industries, is the perfect choice of mold release agent [20]. Silicone oils is made by hydrolysis of dimethyl dichlorosilane with water to produce a primary polycondensation ring. The cyclosomes are cracked and rectorized to get low cyclosomes, and then the cyclosomes, head capping agent and catalyst are put together to get a mixture of different polymerization degrees, and the low boiling matter can be removed by vacuum distillation to get silicone oil. Silicone oils and their derivatives are suitable materials for polyurethane release agents, which possess excellent release properties, such as aluminium alloy mould release agents consisting of silicone oil, overpressure lubricant, emulsifier and water release agents. Silicone oils and their derivatives have been proven to have excellent release effects for many years. However, if the product is reprocessed, the silicone oil-based release agent will have the disadvantages of less frequent release, easy separation of air bubbles on the product surface and cumbersome post-treatment [6]. Dimethylsilicone oil is a transparent liquid, non-corrosive and physiologically inert. It also has excellent resistance to freezing, heat and oxidation, and can be used for a long time in the temperature range of -50°C to 200°C. In addition to the properties of methyl silicone oil, methyl hydrogen-containing silicone oil can also be cross-linked at low temperatures under the action of metal salt catalysts and form waterproof films on the surface of various substrates. As the main ingredient of water repellent, anti-adhesive and anti-corrosion agent, and widely used in the surface treatment of textile, leather, paper, metal, glass, wood and other materials. Hydroxyl silicone fluids are methyl silicone fluids capped with hydroxyl silicone fluids. It therefore has special properties due to the active hydroxyl group. It is a processing aid for silicone rubber and can improve the processing properties of silicone rubber. Sewing thread silicone oil is a compound of large molecular weight polysiloxane and liquid paraffin. Therefore, when lubricating sewing threads, it gives them good lubricity, anti-static properties, friction resistance and smoothness. Silicone oil release agents can be divided into solution type silicone oil release agents, oil paste type silicone oil release agents, aerosol type silicone oil release agents and emulsion type silicone oil release agents according to their form. Solution type silicone release agents are formulated by mixing silicone oil and other additives with organic solvents. Depending on the type of silicone oil, its viscosity and the type of additives used, it can be divided into a number of different types. They are mainly used for shell and film casting, die casting and the moulding of rubber and plastic products. Different kinds of silicone oil are the main component of the solution-type silicone oil release agent, but also can add a variety of wax, clay, MQ-type silicone resin, tale and other ingredients to improve the performance of the release agent, such as dimethyl silicone oil and MQ-type silicone resin mixed with organic solutions to prepare the solution release agent, to improve the mold release durability has very good results. Silicone oil is the main component of the solution-type silicone release agent, but can also add a variety of waxes, clay, MQ-type silicone resin, tale and other ingredients to improve the performance of the release agent. For example, dimethyl silicone oil and MQ type silicone resin mixed with organic solution to prepare the solution release agent, to improve the mold release durability has a very good effect. Paste-type silicone release agents are pastes made by mixing silicone oil with precipitated silica or fumed silica. Compared to oil and emulsion silicone release agents, oil paste release agents are widely used in high temperature and high pressure moulding because of their higher heat resistance and long-lasting release properties. At the same time, the release agent is also suitable for the vulcanisation of bent rubber hoses due to its good lubricating properties. Aerosol silicone release agents consist of methyl phenyl silicone, dimethyl silicone or long chain alkyl silicone as the active ingredient and are sealed in an aerosol can with Freon-11, Freon-22 or Freon replacement. Pure silicone oil release agents are not easy to use, and the release effect is not satisfactory. The solution type release agent also has the danger of fire and poisoning, so the development of emulsion type release agent, and has become the mainstream of the current release agent products. Emulsion release agent can be prepared by mechanical emulsification, that is, silicone oil and water dispersed under the action of emulsifier. It can also be prepared by emulsion polymerization, that is, polysiloxane in the emulsifying agent, catalyst, emulsion polymerization in water system. The emulsifiers used in the latter can be non-ionic, anionic and cationic, but in mechanical emulsification methods, mainly non-ionic emulsifiers are used. The emulsification devices are mainly homogenisers, colloid mills or high-speed stirrers. The silicone oil content of the emulsion products produced is generally 30% to 60% (mass fraction). Further dilute with water to an emulsion with a silicone oil concentration of 0.2% to 1.0% (mass fraction) before use. The diluted emulsion becomes less stable and should be used up as soon as possible. The emulsion release agent has advantages in terms of cost, fire resistance and hygiene, which makes it highly competitive in the market. However, it also has three disadvantages, namely the volatility of water is too poor to be used as a low-temperature mould release agent; poor wettability of the substrate, especially for polymer materials; and the use of emulsifiers reduces the precision of the product. If
ordinary hard water is used constantly to dilute the emulsion, scale will form on the surface of the mould, which will further affect the accuracy of the product if it is not cleaned regularly, so it is better to use soft water to dilute the emulsion. In emulsion type products, some are made by adding organic solvents to reduce the amount of emulsifier used to achieve faster water evaporation and reduce the deposition of solids on the mould surface. Wen Jianqiang[21] used methyl silicone oil and methyl phenyl silicone oil as the main raw materials, and stearamide and polyvinyl alcohol were added. After mixing, heating and stirring, emulsification and other steps, developed a kind of silicone oil demoulding agent with excellent demoulding effect, safe and environmental protection, and can extend the service life of moulds, which was suitable for the demoulding of rubber hoses and printing production[22].

3. Wax release agents

A variety of compounds such as oils, waxes, soaps and macromolecular compounds can be used as active ingredients in release agents. There are two main forms, one of which is to make an emulsion of molten paraffin wax in the presence of an emulsifier and then apply it to the formwork for use. The other way is to dissolve the paraffin wax in solvent oil to make a paraffin oil release agent. This release agent has an ideal release effect, but it is not easy to dilute and apply evenly when the temperature is too low; it is flammable, volatile and unsafe to use, and cannot be stored in the open air. Paraffin wax release agents with high wax content often leave residues of paraffin wax on the concrete surface, which affects the further decoration of the mould surface. The mechanism of action of such release agents is isolation and lubrication. Due to the adhesive nature of the isocyanate in the main polyurethane material, a suitable wax release agent is used to prevent it from bonding to the mould during the moulding process. Wax emulsions can be well used in environmentally friendly waterborne polyurethane release agents, which can reduce the surface tension of the coating and increase the film-forming properties of the release agent on the mould surface, improving the bonding and finishing properties of polyurethane products. This type of release agent, has excellent release performance. Thin film thickness (0.1–1 μm), high dimensional accuracy of products, dry coating, less adhesion to products, not easy to adhere to moulded products, can be diluted with water for use, environmentally friendly, no VOC emissions, can be applied to more difficult to release epoxy resin products. Waxes have a high melting point, good viscosity and excellent film-forming properties, and contain polar groups such as hydroxyl and carboxyl groups that are easily emulsified, making them a very important class of active ingredients for release agents. The film formation process of emulsions is divided into three processes: filling, fusion and diffusion. The low melting point of paraffin waxes gives them good solubility in polymers and improves their fluidity, helping to complete the three stages of filling, fusion and diffusion and to form continuous and homogeneous films, making waxes a suitable material for film-forming materials[23]. Polyethylene emulsion is a non-ionic AC polymer combination of polyethylene copolymers fused into an emulsion by high pressure. It is a non-toxic, odourless and non-corrosive non-ionic emulsion, easily soluble in water, with good resistance to acidity, alkalinity, electrolysis, bathing with resin, not easy to stratify and coalesce. The emulsion is constant in composition, has good chemical stability and does not delaminate for long term storage. It is widely used in the production of water-based inks, liquid shoe polish, metal release agents and other industries. It is an excellent release agent for a wide range of applications in the polyurethane industry and other special industries.

Zeng Xiangyun [24] et al. developed a polyurethane wax release agent by using release wax, paraffin wax and microcrystalline wax as the main raw materials and adding foam stabilizers and petroleum-based solvents. It has the advantages of good release effect, no pollution, no corrosiveness to the mould surface and can be used repeatedly, etc. It is suitable for the release of polyurethane high resilience foam. Gao Huijiang and Xu Yingying[25] et al. took beeswax and rice bran wax as raw materials, added vegetable oil, silicone oil and talcum powder, etc. After hydrolysis and emulsification, they successfully developed a wax release agent with low cost, reasonable components, and safety and environmental protection, with excellent lubricity and good demoulding properties. The method is reasonable, easy to implement, low cost and suitable for large-scale application in the industry.

4. Fatty acid based release agents

Fatty acids and their soaps are very versatile lubricants and can also be used as release agents. They are available from a wide range of sources, are inexpensive, have good compatibility with many plastics, are heat stabilised and are generally pre-mixed with resin prior to processing and are easy to use. Stearic acid is still one of the most important lubricants because of its low price, comprehensive performance and ease of processing into various metal soaps such as zinc stearate, dull, lead, magnesium, barium, cadmium, aluminium, sodium and lithium are all commonly used lubricants. Fatty acid release agents are mainly composed of high-grade fatty acid esters, fatty acid salts, other additives and water and are widely used in the processing of foam moulded products. The fatty acid derivatives are compatible with the rubber compound and their use is not detrimental to the physical properties of the compound. Therefore, this type of release agent can promote the mobility of the rubber in the mould cavity during the vulcanisation of SBR and EPDM moulded products, and can also improve the sliding and lubricating properties of rubber seals and gaskets, and can improve the self-lubrication of reciprocating seals. Thus, the release and processing properties of thermoplastic elastomers such as SBR, EPDM, butadiene rubber, acrylate rubber,
epichlorohydrin and thermoplastic elastomers can be effectively improved in order to obtain optimum economic efficiency. Used in many other elastomers, it has also been found to improve the flow of the rubber in the mould cavity, reduce operating temperatures and shorten the production cycle time of the product. Jin Minglin and Xu Shi [26] developed a wet molding release agent for magnetic materials by using advanced fatty acids as the main raw material and paraffin as the medium, after heating, stirring and emulsification. The release agent can be evenly distributed on the surface of the mold, which greatly improved the release of the magnetic material blanks and made the surface of the products highly accurate and smooth, and it was a green and environmentally friendly release agent as it is pollution-free and harmless to the health of the operators when used.

5. Conclusion
Mold release agents are divided into water-based release agents, oil-based release agents and powder-based release agents. Water-based release agents are widely used because they have the advantages of low price, good release effect, green environment protection, smooth casting surface, good air tightness and good automaticity operation. According to the effective release material in the mold, release agent can be divided into silicone oil type, wax and fatty acid type water-based mold release agent. The water-based release agent has excellent performance, green environmental protection, good plasticity, suitable price, has a broad market prospect and is widely used. The development and research of water-based release agent have been carried out for many years in foreign countries. Quite a number of products have been produced and the industrial chain is becoming mature. Due to the late start of China's research on water-based release agents, there is no systematic research on water-based release agents in China, and there is still a large gap with foreign countries. The high-end water-based release agent is basically monopolized by foreign countries, with the continuous development of mold release technology, the domestic water-based release agent in some degree has been able to compete with foreign, I believe that in the future, China's mold release agent technology will continue to break through, and then break the monopoly of foreign situation.

Acknowledgments
Thanks to the following funds for supporting this project. Postdoctoral Innovation Project of Shandong Province (202103051), Heilongjiang Provincial Natural Science Foundation of China (LH2020E089), China Postdoctoral Science Foundation (2021M691970), University Nursing Program for Young Scholars with Creative Talents in Heilongjiang Province (UNPYSCT-2018205), Fundamental Research Fundation for Universities of Heilongjiang Province (2018-KYYWF-1598).

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