Current Situation And Development Trend Of Silicon-Containing Leather Materials

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Abstract: Organic and inorganic silicon-containing materials are widely used in leather chemisty due to their unique physi-　cal and chemical characteristics.The application and developing tendency of silicon containing materials in leather chemistry was reviewed ,including waterproof material ,fatliquor ,tanning agent ,finishing and leather auxiliary materials etc.

Keywords: silicon containing materials; leather; application; development

Silicone material is the first element polymer material that has been applied in industry with rapid development of application, including many varieties of 4 families such as silicone oil, silicone rubber, silicone resin and silane coupling agent.Due to the high dissociation energy of the silicon-oxygen bond on the main chain, it has a sudden heat resistance. At the same time, due to the low intermolecular force and the high molecular compliant state, it has a small dielectric constant, low surface tension and glass transition temperature. In addition, it also has the characteristics of physiological inertia, air permeability and hydrophobicity, so that it is widely used in leather and its products, light industry and crafts, plastics and composite materials, daily chemicals, textile industry and other fields.

At the same time, inorganic silicon-containing materials, especially ultrafine and nano-powder silicate and amorphous silicon dioxide, are also being studied in depth in the application of leather materials due to their unique structure and properties (such as tanning and filling properties, etc.) and environmental friendliness. In this paper, the research and application of silicon-containing materials in leather making are reviewed in the following aspects.

1. SILICONE LEATHER WATERPROOFING AGENT

Nowadays, waterproof has gradually become one of the most important use values of leather, especially shoe leather and garment leather require the entire cross section to be waterproof. Waterproofing is one of the most important functions of silicone, and its other applications involve more or less hydrophobic or waterproof functions. Leather waterproofing can be done by surface treatment, wet processing, or a combination of the two.

As far as materials are concerned, they can be divided into two types: closed and open. Closed waterproof means that the waterproof material is filled between the leather fibers, and after contact with water, it absorbs water and expands, preventing the further penetration of water, such as grease, paraffin and long chain alkenyl superic acid; Open waterproofing means that some hydrophobic compounds combine with the skin fiber to form a hydrophobic film on its surface, Significantly reduce the critical surface tension and improve the wetting Angle between the fiber surface and water to make water beads impassable, such as fatty acid chromium complexes (AC, CR, etc.), long chain binary carboxylic acids such as sebacic acid and its various derivatives, metal salts of azelaic acid (such as Bavon D), fluorine compounds and organosilicates .

The reason why silicone materials can be widely used in leather waterproofing is that they have low surface tension, and their polar groups combine with the hydrophobic alkyl group of the leather fiber to form a discontinuous hydrophobic film on the surface of the leather fiber, which does not affect the "breathing" performance of the leather, that is, air permeability and water permeability.

At the same time, it can smooth the leather fiber and improve its softness. In the 1970s, the former Soviet Union studied the pre-leaching of leather with 10%Ti(OBu) solution using titanium salt as the curing catalyst by step-by-step waterproofing treatment and then using 45:50:10 polydimethylsiloxane (PMS-200): Ethyl hydrosiloxane: $Ti(OBu)_4$ The second maceration of the mixture significantly improves the water resistance of the leather. In the waterproofing of chrome tanning suedleather, the copolymer of 2% to 3.5% polyethylenedionic acid was used instead of $T(OBu)_4$ in the siloxane solution. It further improved the waterproofing effect when the copolymer was used instead of Ti(OBu). , the effect is better.

At present, the most promising silicone waterproof material for leather is generally water-emulsion type, which is commonly prepared by external emulsification method. It is the (methyl, hydroxyl, hydrogen-containing or amino, etc.) silicone oil directly mixed with emulsifier, water and adding agent by emulsifying equipment processing emulsion. Among them, hydrogen-containing silicone oil has the best application effect. According to reports, BASF's silicone water repellent Densodrin S is made using this method.

Since then, a new waterproofing agent Xe-roderm DS has been developed. The main components are paraffin wax and siloxane, which can be used to achieve the best waterproof effect when the chrome tanned leather is completely neutralized. In addition, in order to improve the durability of organosilicon materials, most of the domestic use of active organosiloxanes, the introduction of active reaction groups, so that it can be combined with the skin fiber.

For example, Chengdu Organic Silicon Research Center of the Ministry of Chemical Industry, through the polymerization reaction to obtain silicone modified acrylic polymer WPT-st1], with organic silicon modified natural oil to prepare WPF-w3] respectively applied in leather retanning and fat, and then with metal salt sealing carboxyl group, to obtain good performance waterproof leather. The application range of silicone waterproof material in wet treatment section after tanning is further widened. In addition, a polysiloxane waterproofing agent that does not need to be fixed has been developed abroad and has applied for a patent.

The product will self-inhibit the concept of the introduction of polysiloxane is either in the emulsification system of polysiloxane containing carboxyl group, the introduction of self-inhibited anionic emulsifier containing cyanuric acid group, when drying or losing counter-ions, the emulsifier forms a water-insoluble dimer or oligomer, which is precipitated, or the synthesis of a new polysiloxane emulsifier containing cyanuric acid group.

It has the characteristics of PH-sensitive phase separation, and these two types of products are made of water-repellent agents combined with parental polyacrylate dispersion and wax emulsion, and the waterproof effect is better. Leather is water resistant according to DIN 53338 and its penetration time is all higher than 0.5h Roughs.

Since this kind of waterproofing agent does not need to be fixed with chromium salt, it will not cause water pollution, which is more in line with environmental protection requirements and feels more comfortable and rich in silk. Of course, the waterproof effect is not only directly related to the waterproof agent, but also has an important relationship with the treatment method and the process balance before and after. If the whitened wet blue leather must be fully washed to remove the hydrophilic substances used in the previous process as far as possible, the subsequent wet processing section should use as little surfactants as possible, especially non-ionic surfactants and so on.

2. SILICONE LEATHER GREASE AND SOFTENER

Fatting is an important process in leather production. Treating leather with fatting agent can form an oil film on the surface of collagen fiber, so that the finished leather has certain physical and mechanical properties such as softness, fullness and elasticity. Mainly used a variety of natural plant oil modification products and related synthetic products. It often contains a variety of other additives to give the leather waterproof, oil resistant, anti-fouling, flame retardant, anti-fogging and other specific performance required. Organosilicide has lower surface tension and better hydrophobicity, it is one of the first materials to prepare leather waterproof grease agent, and its fat after the leather is especially smooth and soft, and can become a better softening agent.

Most of the early silicone grease agents were solvent-based, and the silicone waterproof grease agents developed and widely used before the project were mainly water-emulsion type, and active organosiloxanes were mostly used to increase the combination of silicone with grease and skin fibers. Foreign research on silicone leather waterproof grease agent is earlier, there are a number of companies to produce series of products, For example, BASF Densodrin series, LANXESS Xera-DERM series and Schill &Seilach Per-fectol series, the leather processed by them meets the requirements of waterproof leather. In China, the following two technical routes are mainly used to synthesize silicon-containing grease materials:

① By introducing carboxyl group, amino group and other active groups on the organic silicon compound molecules, it has the binding and self-emulsification. BP1005475 reports a water-soluble silicone softener, which is made up of an alkoxy amine silane and a hydroxy-terminated polydimethicone. The softness and fullness of the leather after treatment are very good, but it needs to be catalyzed after this treatment.

② The organic silicon is grafted on the natural oil or synthetic oil molecular chain. The silicon-containing fat additive prepared by these two methods has a good combination effect with the leather fiber, and effectively overcomes the problem of easy migration of silicone in leather. At the end of the 20th century, Wang Bao and 9-13] et al. used modified vegetable oil, alcoholized peanut oil, modified corn oil, natural soybean oil and sunflower oil as raw materials, respectively.

The anionic leather fatening agent was prepared by grafting modification with active organosilicon. The softness and smoothness of the leather after fatening with these products were better, and the amount of fat could be reduced to different degrees. In recent years, Xiong Jing et al. [14] developed DSF-W compound silicon-containing fatting agent, which is prepared by grafting silicone with vegetable oil and introducing a group with binding properties to collagen through sulfite.

Application tests have proved that this kind of fatting agent has good stability, strong binding properties and acid and alkali resistance. Good permeability, making the finished leather soft, silky and oily feel. Luan Shouting et al. [1]5] prepared a compound derived from the grafting polymerization of natural plant soybean oil with dimethyldichlorosilane, an organosilicone monomer containing active groups, as the main component, and the product was obtained by connecting hydrophilic groups and complex emulsification. The finished leather treated with the fatening agent has smooth grain surface, fine, soft and comfortable hand feel similar to silk, and can enhance the waterproof and anti-mildew properties of the leather, and can be used for fatening of suede leather and front garment leather.

Although there are many researches on silicon-containing fat additives in China, it is still quite difficult to produce products with suitable price, stable storage and sudden performance, and few varieties are really applied on a large scale. Therefore, it is necessary to conduct in-depth research in this area to meet the needs of the domestic market.

3. LEATHER TANNING AGENT CONTAINING SILICON

As early as the 1960s, the Carbide Company in the United States issued a patent, reporting that siltrioxane has a tanning effect, and can obtain a good waterproof effect of leather, its most significant advantage is that the leather made of boiling water, still maintain good flexibility. British patent BP 822862 reports that organosilicon compounds and chromium chloride or basic chromium chloride can react in a certain alcohol solution, and then the products obtained by hydrolysis tanned leather waterproof effect is very good. In recent years, people have done a lot of research on tanning leather with nano SiO_2.

Using collagen as a model, Fan Haojun 16 et al. investigated the binding mode of nano SiO_2 with protein and its effect on protein properties. The results showed that nano SiO_2 can significantly improve the hydrolytic stability of collagen in the presence of enzymes, acids or bases. The shrinkage temperature of alkali skin can reach 95℃ or more when treated with 0.3% nano SiO_2 (based on the mass of alkali skin).

Although the mechanical properties of the leather tanned by this method are not as good as those tanned by chromium salt, it is superior to chrome tanned leather in yield, grain condition, fullness, softness and washeability. In addition, in order to reduce the amount of chromium and further improve the tanning system, chrome-zinc-silicon composite metal tanning agent was prepared and optimized abroad, so that the shrinkage temperature of tanned leather reached about 95℃, the absorption rate of chromium reached 90%, and the mechanical properties and wearing comfort were comparable to or better than that of chrome tanned leather .

In addition, the complex-tanning agent of aluminum-tannic-silicon has been studied, which can be used without acid immersion. The relative molecular weight of the tannic acid used here is lower than that of plant tannin, which can avoid the deficiency of plant-tanned leather. The aluminum contained in the tannin can form a complex with the tannin, which can improve the wet and thermal stability of the leather while maintaining the color of the original leather. The silicon can improve the softness and wear resistance of the finished leather, and the shrinkage temperature of the finished leather can reach 95℃.

The analysis of its impact on the environment shows that the aluminum absorption rate can reach 98%, and the COD and TDS values are significantly decreased 18. At present, the awareness of environmental protection in the world continues to strengthen, everyone is seeking chromium-free, less chromium tanning methods, while the need to develop waterproof, washeable leather if organic silicon and nano SiO_2 should be used in the development of tanning agents, aid tanning agents and retanning agents, there may be new discoveries.

4. SILICON MODIFIED LEATHER FINISHING MATERIAL

Finishing agent mainly includes film forming agent and coloring agent According to the requirements of coating film forming performance, there are also additives such as penetrant, plasticizer, leveling agent, crosslinking agent, rheological agent, feel agent. At present, a large number of literatures show that silicone can be used to modify traditional leather finishing materials such as acrylic resin, polyurethane resin and nitrocellulose to improve their comprehensive properties. Acrylic resin has good blending with pigment and other resin, the film has light resistance, water resistance, abrasion resistance and scratching resistance, has good elasticity, toughness and softness, good adhesion and other advantages. However, the resin has poor temperature resistance and is prone to hot sticking and cold brittleness. Silicone has excellent temperature resistance, softness and smoothness, so it can be used to modify acrylic resins.

The modification route can be divided into two kinds due to the different organic siloxane active groups used for modification:

① The graft copolymer is formed by condensation reaction between siloxane with hydroxyl group and acrylic acid resin with hydroxyl group;

② Siloxanes containing double bonds, especially siloxane oligomers containing double bonds, are copolymerized with acrylic monomers to form comb polymers containing siloxanes in the side chain or copolymers containing siloxanes in the main chain. Among them, the former generates the Si-0-C bond, and the latter generates the Si-C bond.

The preparation process of the former is simple, but its hydrolysis stability is not as good as that of the latter. Rohm &Haas patent CN1039430A describes a stable water emulsion copolymer with controlled siloxane crosslinking for leather top finishes. The product was obtained by emulsion polymerization of butyl acrylate, acrylonitrile, methacrylic acid, methylpropenoxy propyl trimethylsilane, and D_4 as reactants in aqueous solutions of dodecyl benzene sulfonic acid and ammonium persulfate. The leather film obtained by coating with the copolymer is wear-resistant and non-brittle at low temperature.

In an emulsion system and slightly acidic condition, D_4 ring-opening polymerization and acrylic radical polymerization were applied to form a synchronous interpenetrating network polymer. The resulting composite membrane showed good high and low temperature resistance, hydrophobicity, and solvent resistance. It significantly improved the touch and brightness of the coating.

Zhang Xiaolai et al. Used the monomer post drop addition to synthesize the organosilica-acrylate copolymer using D_4 and γ-methacryloxysilane by emulsion polymerization. The effects of different organosilicon content on the film forming properties, film tensile strength and film elongation of copolymerization products were investigated. Polyurethane finishing agent can form a smooth smooth film on the leather surface, friction resistance, excellent weather resistance, soft and elastic, and strong adhesion. However, due to the large molecular chain of aqueous polyurethane containing more hydrophilic groups, the water resistance of the film is poor. Silicone has good water resistance, but its compound film has poor adhesion to leather.

Therefore, the use of silicone and polyurethane copolymerization can be used to obtain an ideal finishing material. Wang Wusheng et al. synthesized siloxane-terminated linear polyurethane dispersions with γ-aminopropyl triethoxysilane, TDI, polycaprolactone diol, etc. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) studies showed that the dispersion could be further cross-linked during film formation and drying. If the polyurethane microgel was further cross-linked with water-soluble epoxy siloxane after film formation, a high-performance organic coating could be obtained.

Tan Zhengde et al. reacted the prepolymer obtained from the reaction of polyether and tertiary amine with diaminopropyl polydimethylsiloxane and a small amount of dihydroxymethylpropionic acid to prepare cationic modified polyurethane emulsion. Active groups were introduced into the soft segment to strengthen the interaction between the soft and hard segments, and the product could be used as a top coating agent.

In addition, Dandong Light Chemical Research Institute also used organosiloxane and acrylic resin to carry out emulsion grafting modification of nitrocotton Junlan Wang et al 261 took water-based polyurethane emulsion with core-shell structure as seed emulsion to further react with acrylic ester and organosilicon to prepare soap free copolymerization emulsion; Haihong Wang et al. also synthesized silicone modified acrylic polyurethane emulsion with core-shell structure.

The finishing agent obtained has the advantages of three kinds of polymers. Inorganic silicon-containing materials such as ultra-fine silicates and nano SiO_2 are expected to be effectively applied and have broad development prospects. Ma Jianzhong et al. prepared SiO_2 sol by sol-gel method using acid and base as catalysts, and then combined it with acrylic resin to prepare modified acrylic resin finishing agent. When the product is used for leather coating, it is found that the water permeability and gas permeability of the finished leather are significantly improved than that of the leather coated with unmodified acrylic resin, and the folding fastness is more than 100,000 times.

When alkali was used as catalyst, the water resistance and solvent resistance of the composite coating were increased by more than 55%. Polymer/layered silicate nanocomposites are organic, inorganic and nano characteristics in one, with excellent mechanical, permeability resistance and conductive properties of the composite material, if it can be applied to leather coating, it is expected to have heat resistance, flame retardant, light weight and other properties of special fire or military leather products.

5. SILICONE LEATHER FINISHING AID

Hand feel is an important index to measure the quality of the finished leather. The use of additives that can improve the hand feel can obviously improve the surface properties of the finished leather.

At present, the handle agents used in tanneries mostly contain wax and organosilicon. Due to the variety of imported products, complete style, stable quality, can meet the needs of a variety of styles of leather products.Therefore, the market of hand feel agent is mostly occupied by foreign companies. Many products have also been introduced in the country. They are either wax-based sensing agents and slip agents, or special feel agents made of silicone as raw materials.

However, if they were prepared by the D_4 ring-opening polymerization and emulsification process, the relative molecular weight of the product was small and easy to be moved, resulting in non-durable defects. Using a variety of natural waxes and organic silicone oil as raw materials, Lou Shouqiang appropriately added a certain amount of surfactants and other substances, and obtained a stable silicone and waxy leather top coating with interface complex formation and PIT method. Wang Jiatu et al. used a complex emulsifier system to emulsify macromolecular organosiloxanes, thereby producing a handfeel agent with excellent smoothness and oily feeling.

In this laboratory, macromolecular hydrogen-containing silicone oil was used as raw material, modified by hydrosilane addition reaction, and then emulsified to produce carboxyl modified silicone oil emulsion with narrow particle size distribution and good compatibility with paraffin and organic resin, which can improve the durability of the material without affecting the characteristics of silicone itself. In addition, if the fluorofluorocarbon chain is properly introduced into the silicone main chain, the obtained silicon-fluorine composite material will have excellent lubricity, hydrophobicity, oilophobicity and anti-fouling properties.

6. LOOK FORWARD

With the continuous improvement of people's living standards, the quality requirements for leather and its products are also getting higher and higher, highly soft, good feel, and waterproof leather products are more and more favored by everyone. The authors believe that silicon-containing leather materials will develop in the following directions:

(1) Emulsification will develop in the direction of low surfactant use. When emulsifying silicone oil, especially unmodified silicone oil, it is very difficult, and the amount of surfactant is large, generally up to 20% of the quality of silicone oil, but too much surfactant will cause a certain negative impact on the quality of leather.

(2) The development of salt-free fixed polysiloxane waterproofing agent. Carboxyl silicone oil plays an important role in leather waterproofing, retanning, fatting, etc., but it must be fixed by metal salt in the later stage of processing, which not only increases the pollution of metal ions, but also affects the grain feel of the finished leather.

(3) The development and application of new silicone surfactants in leather. Because of their unique surface activity, organosilicon surfactants have been used in the preparation of nanostructured materials, including template inorganic materials and capsules. The latest data show that its application in leather degreasing and hair removal can simplify the process of salt skin or fresh skin wet processing section and reduce the pollution of sodium sulfide and protein solution produced by hair destruction. Its application in improving the quality of finished leather and reducing pollution has attracted more and more attention in the industry.

(4) The application and development of water-soluble silicates in leather water farms. In recent years, a lot of research work has been done on the application of water-soluble silicate in leather water treatment abroad. It can replace lime and sodium sulfide for hair removal and liming process. The processed leather can be directly used for cutting without pre-tanning process and is beneficial to the absorption of materials in the post-process reduces the discharge of solid and liquid waste. However, the domestic research in this area is still close to the blank stage.

TAKE PART IN THE ESSAY

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