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One Stop Silicone Solution

The Application Of Silicone In Leather

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Disclaimer: The following silicone Leather industry standard was translated from Chinese Language standard version. Due to Language habits and the translator's personal English Level, there may be some inaccuracies.

Abstract: The properties of silicone and its main applications in leather industry are introduced. It is mainly used as waterproof agent, tanning agent, fatting agent and finishing agent for leather. In this paper, the main manufacturers and product properties of silicones at home and abroad are summarized. Some suggestions on the future development of silicone leather materials were put forward, and the prospect of their application in leather was prospected.

Keyword: Organosilicon; Leather; Apply; Suggestion

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With the continuous improvement of people's consumption level, people's requirements for leather properties are becoming higher and higher. The study found that adding some additives to the leather can significantly improve the quality of leather products, and give the leather some new properties, making the leather surface more smooth, soft, full and elastic. Silicone material has the basic properties of low surface tension, low viscosity temperature coefficient, high compressibility, high gas permeability, and has the excellent characteristics of high and low temperature resistance, electrical insulation, oxidation resistance stability, weather resistance, flame resistance, water repellency, corrosion resistance, non-toxic and tasteless, and physiological inertia, etc.

These excellent properties have laid a solid foundation for its application in leather. It is an important direction for the development of leather chemicals. Foreign research on silicone leather materials is relatively early, and the properties of silicon-containing leather additives developed are better. The domestic research on silicone began in 1952, although compared with developed countries started late, but through the unremitting efforts of leather workers, has developed a lot of excellent performance of silicon-containing leather materials, some of which have reached the international advanced level. However, in general, the domestic silicone leather materials compared with foreign countries, both in the variety and performance there is a big gap, especially

some multi-functional, efficient leather additives are relatively empty or white, so to a large extent still rely on imports, which is also the current stage of the domestic leather workers need to note the problem.

1. CHARACTERISTICS OF SILICONE COMPOUNDS

1.1 STRUCTURE OF ORGANOSILICON COMPOUNDS

Organosilicon compounds refer to molecules containing the element silicon, and the silicon precursor is connected to the organic polymer, it is also common to those compounds through oxygen, sulfur, nitrogen so that the organic group and silicon atoms are connected called organic silicon compounds. Silicone compounds have a unique structure:

1. Sufficient methyl groups on silicon atoms can shield the high-energy polysiloxane main chain;
2. the carbon-hydrogen bond is non-polar, so that the interaction between molecules is very weak;
3. The silico-oxygen bond length is longer and the bond Angle is larger; High bond energy, good thermal stability;
4. The silico-oxygen bond is a covalent bond with 50% ionic bond characteristics.

1.2 CLASSIFICATION OF ORGANOSILICON COMPOUNDS

With the rapid development of silicone science and technology, the types of silicone products are increasing day by day, and the classification methods are different. According to the molecular structure, it can be divided into ring polymer, linear polymer, ladder polymer, cage polymer, tree polymer and three-dimensional network polymer. According to the main chain structure of the molecule, it can be divided into polyorganosiloxane, polysilane and heterochain organosilane polymers. According to the product form classification can be divided into silicone oil, silicone rubber, silicone resin and silane coupling agent four categories. According to the product classification can be divided into release agent, defoamer, lubricant, sealant, fabric finishing agent, polish, adhesive and so on. According to the product classification can be divided into release agent, defoamer, lubricant, sealant, fabric finishing agent, polish, adhesive and so on.

1.3 PROPERTIES AND USES OF ORGANOSILICON COMPOUNDS

Organosilicon compounds contain both "organic groups" and "inorganic structure", and this special composition and molecular structure make it integrate the characteristics of organic matter and the function of inorganic matter in one. Compared with other polymer materials, the most outstanding properties of silicone products are: temperature resistance, weather resistance, electrical insulation performance, biological characteristics, low surface tension, in addition to air permeability, hydrophobicity, softness, wear resistance and other special points.

These excellent properties can not be compared and replaced by other organic polymer materials, so it has been widely used in aerospace, electronics and electrical, light industry, chemical industry, textile, leather, machinery, construction, transportation, medical and health, industrial and agricultural production, emerging technologies and People's Daily life. Silicone products have become one of the fastest growing and most widely used varieties of new chemical materials.

2. THE APPLICATION OF SILICONE IN LEATHER

2.1 LEATHER WATERPROOFING AGENT

The silicone used in leather processing materials is mainly polysiloxane (such as silicone oil, silicone rubber, silicone resin, etc.), mainly used as leather tanning agent, fat agent, water repellent, antifouling agent, brightener, preservative, feel agent, slippery agent, etc. The comprehensive properties of organosilicon are constantly reflected in leather auxiliaries, making it a hot spot in the study of leather chemical materials at present. Leather waterproof has always been a concern of people, it directly affects the quality of leather. Silicone surface tension is small, and after binding with the leather fiber, can greatly reduce the surface tension of the leather, so that the treated leather has good hydrophobicity, but also give the leather soft, smooth and other properties.

Foreign research on silicone water repellent is earlier, there are many companies producing series of products. Such as BASF company's silicone water repellent Densodrin S and new water repellent Xeroderm DS, the main components of Xeroderm DS are paraffin and siloxane, in the case of chromium tanning agent neutralization, with its treatment can achieve the best waterproof effect. Japan Shin-etsu KF99

hydrogen-containing silicone oil is a colorless transparent liquid, with weather resistance, good hydrophobic effect and other characteristics, can be catalyzed by some metal salts crosslinked film, with moisture-proof, mildew proof, rust proof function, widely used in leather moisture-proof, waterproof treatment.

Toshiba's TSF484 silicone oil is odorless and non-toxic. Under the action of catalyst, it can be cross-linked at the appropriate temperature to form a waterproof film on the leather surface, which is a better waterproof agent. Although the water resistance of these products is better, but much needs to be fixed by chromium salt, the addition of chromium to the environment has brought a certain pollution, and will pose a certain threat to the health of people and animals, so the development of chromium-free environmentally friendly leather waterproof agent has become an inevitable trend of development.

Recently, Bayer company invented a silicone based XerodermP-AF and XerodermS-AF waterproof material, which not only has good waterproof performance, but also only needs to be fixed with formic acid and has no pollution. Domestic research on silicone leather waterproof agent is late, but there are some excellent waterproof materials, such as Dongguan new silicon industry Polymer Material Co., LTD. SR series waterproof agent, can form a special structure of waterproof, water-repellent skin film on the surface of the leather, giving the leather good water resistance and washable resistance, its waterproof performance is durable. It will not change the permeability and feel of the leather.

The long chain alkyl silicone wax produced by Shanghai Joule Wax Company has excellent properties, which can be divided into solid and liquid, and the treated leather has good waterproof effect and good hand feel. WPT-S waterproof grease additive developed by Chengdu Silicone Research Center of the Ministry of Chemical Industry is a kind of multi-functional material with waterproof function. In addition, there are LF-1 developed by Hangzhou Tongda Leather Auxiliary Research Institute, AB-1 by Wenzhou Baobo Chemical Co., LTD., ZWSP by Yuanxi Dongfeng Leather Chemical Plant, SH-H03 by Shenzhen Jipeng Silicon Fluorine Material Co., LTD., these products have excellent waterproof performance. Significantly improved leather properties.

2.2 LEATHER TANNING AGENT

As early as the 1960s, the United States carbon company published a patent report, siltrioxane has a tanning effect, and can obtain a good waterproof effect, and its most significant advantage is that the leather made of boiling water still maintains good flexibility. The United States patent later reported the use of polysiloxane as a tanning agent, but as a tanning agent alone is not good, if used in combination with chromium is significantly effective. The British patent reported that organosilicon compounds and chromium

chloride or basic chromium chloride can react in a certain alcohol solution, and the product is obtained after hydrolysis, and the product is used as a tanning agent, and the waterproof effect of tanned leather is better.

The Chinese patent also reported that polyhydroxyalkylphosphine silicone tanning agent, compared with the existing tanning agent, has lower destructive power to the fur coat and less damage to the hair, the tanned fur has high gloss, high shrinkage temperature and bright color, leather drought resistance, aging resistance, with good dry/wash resistance; Tanned leather does not contain toxic heavy metals such as chromium; Tanning agent will not accumulate in the organism, no carcinogenicity; The production process is simple, easy to control and detect, and can ensure the stability and consistency of products.

Chromium tanning agent has good properties of leather, and the tanning process is relatively mature, so chromium tanning method is commonly used at present, but chromium has brought serious harm to the environment and human body, and non-polluting and low-cost tanning agent has become the key research project of tanners. Chromium-zinc-silicon composite metal tanning agent has been prepared and optimized abroad, and its properties and application effects are comparable to those of chrome-tanned leather.

In China, Fan Haojun, Shi Bi et al. have carried out in-depth research on nano-scale silica, explained its tanning mechanism, and evaluated its tanning agent. The results show that the tanning effect is good. With the deepening of research and the strengthening of environmental protection, chromium-free tanning agents and tanning methods, including multi-metal tanning agents, will become an important research direction.

2.3 LEATHER FATTING AGENT

Fatting is an important process in leather production. A layer of oil film can be formed on the surface of collagen fiber by fatting agent, so that the finished leather has certain physical and mechanical properties such as softness, fullness and elasticity. Silicone is used as a grease agent mainly because it has good lubrication properties, and has a good waterproof effect. Most of the early silicone grease agents were solvent-based.

At present, the water-repellent silicone grease agents developed and widely used are mainly water-emulsion ones, and most of them use active organosiloxanes to increase the bonding between silicone, grease and skin fibers. Foreign research on silicone leather waterproof fatting agent is earlier, and there are many companies producing series of products. Such as BASF's Densodrin series, Bayer's Xerodern series and Schill&Seilach's Perfectol series, these products are integrated with water resistance and grease. The

leather treated by it has a good waterproof effect. China began to study silicon-containing grease in the 1980s, and the focus of the previous research was mainly on using the excellent properties of organosilicon compounds to modify natural oils or synthetic fats.

By introducing carboxyl, amino and other active groups into the organosilicide compound molecules, the prepared silicon-containing grease has binding properties and can be self-emulsified. To overcome the problem of organic silicon migration in leather. Ma Yongxiao, Yang Min, Zhang Zhongcheng, Jiang Hua, Wang Xuechuan and others have prepared silicone leather fattening agent with excellent performance by reacting with different raw materials and silicone materials. At present, although there are more studies on silicon-containing fattening agents in China, there are still few varieties that form a scale, especially cheap and multi-functional silicon-containing fattening agents.

Only a few companies in China produce silicon-containing leather fattening agents, such as DSI silicone sulfite leather fattening agent produced by Guangzhou Xiangke Chemical Co., LTD. It is a new type of chromium-resistant leather fattening agent synthesized by special new process from organic silicon monomer and animal and vegetable oil. The leather fat agent SB produced by Xinhui Xinsheng Chemical Co., Ltd. is composed of natural oil, silicone and a variety of additives.

The product can penetrate into the entire cross section of leather, distribute evenly among the microfibrils, and have a good combination with the leather fibers. Therefore, while making the leather soft, it can also improve the fullness of the leather, has good light resistance, and can avoid the panning of light colored leather.

2.4 LEATHER FINISHING AGENT

Finishing agent plays a very important role in leather production, and the quality and grade of leather after finishing are greatly improved, which greatly increases the commercial value of leather.

Leather finishing agent is generally composed of film forming substance, coloring substance, solvent and finishing additives such as feel agent, slippery agent, softening agent, brightener, anti-stick agent, anti-fouling agent and so on.

2.4.1 Hand feel agent

Hand feel is a very important index to measure the quality of leather. The use of hand feel agent in the top finish of leather can greatly improve the comfort, beauty and added value of leather. Among the hand-feeling agents, silicone hand-feeling agents have the best

effect, the most varieties, the most widely used and the fastest development. The leather after finishing with silicone feel agent can not only maintain elasticity, fullness, permeability and hygiene, but also improve the feel, improve the softness, dry fast after finishing, and it is not easy to harden and become brittle after drying, and the surface of the leather has good stability to water and chemicals.

Additive 2229 handle agent of Rohm and Haas Company is directly compounded with silicone compound and appropriate emulsifier, which can make the leather surface have better smoothness and oily feeling with a small amount, but the price is more expensive. Clariant's Melio 5230 is a polyether modified silicone emulsion with good water solubility. Stahl's HM-183 feel agent is a water-soluble silicone emulsion with good friction resistance and anti-atomization.

At present, domestic tanners have also done in-depth research on silicon-containing handle agents, such as Wang Gaoxiong, Li Linsheng, etc. have made a focus on the synthesis methods of solvent, emulsion, silicone wax emulsion and microemulsion silicone handle agents. In order to overcome the defects caused by the easy migration of silicone, Luo Rong et al. conducted in-depth research on hyperbranched silicone leather feel agent, Wang Jiayu et al. also selected different macromolecular organosilanes as raw materials to produce high-grade leather feel agents with different styles and properties comparable to imported similar products. On the basis of summarizing the scientific research achievements of various handfeel agents in China, Zhejiang Institute of Chemical Industry has successfully developed silicon wax amphitrotic handfeel agent, which can make the leather surface smooth, flexible, soft and comfortable after treatment.

And the production process is simple, the production process does not produce three wastes, is a high-grade feel agent. In addition, there are many companies that produce excellent feel agents, such as the SR series of Dongguan New Silicon Ye Polymer Materials Co, LTD. XT-803 of Shishi Lvyu Chemical Trading Co, LTD., FY-4610 of Guangzhou Fluyuan Silicon Technology Co, LTD., and SI-2056 of Laiyang Shengbang Chemical Co, LTD.

2.4.2 Slippery agent

Silicone leather sliding agent mainly has two kinds: solvent type and emulsion type. Solvent-based silicone sliding agent is to mix the selected silicone polymer with the appropriate solvent and stir evenly, and then add the catalyst to stir evenly to form a sliding agent. However, due to the lack of toxicity and flammability of organic solvents, they are gradually replaced by emulsion silicone leather smoothing agents.

Emulsion type silicone leather sliding agent is divided into compound type and synthetic type. The cost of the compound type of sliding agent is high, and the varieties of silicone products in China are few, and the selectivity is small; The synthetic sliding agent is made of annular siloxane by ring-opening polymerization. This kind of sliding agent feels smooth, full, elastic, natural luster, and relatively low cost, so the focus of domestic research is mainly on the synthetic emulsion sliding agent.

At present, there are many companies producing silicone smooth agents, such as Laiyang Shengbang Chemical Co., Ltd. 2058, Shanghai leather chemical factory 330, Brilliance Chemical New Materials Co., Ltd. GWC-L and so on. Abroad there are Dutch Stahl company KS series, Italy Dicoro company Deasil WIDR, Clariant company Melio WF series, Melio OF series, Persiderm SIN and Zymonol Wax TL from Bayer.

2.4.3 Softener

Leather softener plays an important role in improving the feel, softness and other properties of leather products, and is an essential auxiliary in the process of leather making. Silicone has the prerequisites for being an excellent softener because of its excellent physiological inertia and extremely flexible backbone. If the siloxane is modified with compounds containing ammonia group, epoxy group, hydroxyl group, etc., the modified organic silicone softener with better softening effect can be obtained.

In this regard, a lot of effective research has been carried out both inside and outside the country, for example, Zhou Jianhua and Zhang Xiaolai synthesized a reactive amino silicone oil softener for leather by transesterification reaction using WS-62M and SG-Si900 as raw materials and amine as catalyst. XT-803 from Shanghai Betson Industrial Co., Ltd. consists of a variety of specially modified silicone elastomers, which can be used alone, or mixed with polyacrylates, polyurethanes, etc., to obtain special product properties. SR973, 922 and other softeners of Dongguan New Siye Polymer Materials Co., Ltd. can greatly change the softness of leather, and have good stability, durability, water resistance, lubricity, and compound function, which can effectively improve wear resistance and smoothness, anti-viscosity, etc.

In addition, there are GK-JS of Guangdong Maoming Gangyi Fine Chemical Plant, H80 of Hefei Chemical Research Institute, ND-3 of Jixi Organic Chemical Plant in Anhui Province, SC of Zhuhai Zhongtong Jinxi Chemical Company, FS-L of Dandong Leather Chemical Plant and so on.

2.4.4 Brightener

The use of leather brightener can improve the appearance, health and physical and mechanical properties of leather products to a certain extent, and can not be ignored to improve the quality of leather. The main types of leather brightener are casein brightener, nitrocellulose brightener, acrylic resin brightener, polyurethane brightener and wax-containing silicon-containing leather brightener.

At present, there are many researches on the use of silicone modified acrylic resin, nitrocellulose and polyurethane brighteners at home and abroad, and there are many silica-containing acrylic resin brighteners and silica-containing polyurethane brighteners. The study of silicone leather brightener abroad is earlier, and the product categories are complete and the performance is stable, such as the United States Dow Corning Company JX-2010-12, BASF company Corial Wax EG, Bayer company Persoftal SWA, Stahl company KS series and so on.

In recent years, China has also done a lot of research in this area, and developed a series of excellent performance products, such as the Ministry of Chemical Industry Chengdu Organic Research Center NS-01, Dandong Light Chemical Research Institute DX-8052, Guangzhou Kanggujia Chemical Technology Co., Ltd. KE-507, Shishi Lvyu Chemical Trading Co., Ltd. LY-3501, Dongguan Dalang Changhui Plastic Auxiliary Factory SL-105, Wuhan Obai Technology Co., LTD. YN-5680, Guangzhou Fluyuan silicon Technology Co., LTD. FY-4609 and so on.

3. SUGGESTIONS AND PROSPECTS FOR ORGANOSILICON PEEL MATERIALS

With the continuous improvement of people's living standards, the quality requirements for leather and its products are becoming higher and higher, especially under the gradually enhanced environmental protection requirements, the development of high-quality, high performance, high environmental protection leather chemical materials is particularly important. Silicone has good comprehensive energy, no pollution to the environment, and plays an important role in improving the quality of leather materials and increasing the types of leather materials. Silicon-containing leather materials should be developed from the following aspects:

(1) While not affecting the fullness, softness, permeability and many other excellent properties of leather, the development of chromium-free fixed polysiloxane waterproof

agent is an inevitable trend, but also a very new research field, worthy of our attention.

(2) Increase the research and development of silicone leather tanning agent, and the new chromium-free leather tanning agent is the ideal tanning agent for leather enterprises to achieve the goal of chromium-free production.

(3) The research, development and production of fattening agent should be developed towards multi-function and compound direction, and at the same time, the strong research on the new products with excellent performance that have been developed and the promotion of them should be strengthened to play a role in the tanning production as soon as possible, and ensure the quality stability in the production.

(4) Develop series and multi-functional silicone finishing agents, especially composite finishing agents. In addition, the application of new technology of diplomatic combination and emulsion polymerization can also improve the properties of leather finishing agents to a certain extent, which should attract the attention of tanners at home and abroad.

(5) Leather workers should cooperate with silicone experts in research, which can speed up the pace of development of silicone leather materials, to achieve twice the effect.

With the development of science and technology and the needs of the market, the variety and quantity of silicone compounds suitable for the leather industry are increasing, and other excellent characteristics of silicone are constantly being developed, and the application prospect of silicone in the leather industry is very broad.

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