

Research on Synthesis and Application of Environment-Friendly Leather Chemicals

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Abstract: According to the current situation of environmental pollution in leather industry in our country, the paper analyses the necessity of developing environment-friendly leather chemicals. In view of challenge from pollution, technology and trade barrier, we indicate the basic principle, development tendency and several synthetic techniques of environment-friendly leather chemicals research and development. Several leather chemicals are introduced from Brother Enterprises Co., Ltd.

Key words: leather chemicals; Green Chemistry; research and development; Fatliquor; tanning agent

Summary

In our country's light industry, pollution caused by leather-making, which is obviously confirmed, is second only to that of Pulp & Paper industry. Today more serious topic of conversation being discussed is whether the leather industry could achieve its sustainable development or should proceed in china. Obviously, the question of life and death has added to heavy strain to leather industry. The technology of pollution-reducing and discharge-cutting is only way for leather industry to release the internal pressure and survive.

In addition, China's leather industry is also under enormous external pressure. Over the years, export has been the brightened dot of the leather industry. A large number of enterprises' survival and development have also depended on the export trade. Consequently, the standard of their products for export have been determined by the target country. leading the overall level of civilization, developed countries pay more attention to eco-indicator of consumer goods and set a series of standards for some chemicals forbidden of restriction. Most of these standards exceed the current standard of our country and beyond of most enterprises' technical affordability. Export enterprises, in order to survive, have to try their best to meet those standards. Unfortunately, coincided with the global financial crisis, the significant decline in consumption in developed countries affected negatively export trade of China leather industry.

It is clear that china's leather industry has been beset with difficulties both at home and abroad. Survival or death, or escape, is not a question being difficult to conjecture. What is to be verified is how many we can improve and ultimately how many enterprises we can keep. Actually, according to adjustment and promotion programme for light industry promulgated by the State Council in may, 2009: till 2011 leather-making wastewater and COD emission decreased respectively by more than 15,000 tons and 5 million tons comparing with 2007. At the same time those tanneries whose annual output is less than 30,000 standard sheets will be shut down with a firm hand. In such a simplified but more demanding targets, the direction of change and effort to the leather industry is clear, but the task is extremely arduous.

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1 Demanding of leather industry reducing pollution on environment-friendly chemicals

The pollutants of leather industry can be divided into two major categories according to hazards level and difficulty level to deal with: The first pollutant is Oils and fats, meat residue, hair and edge waste coming from raw leather, amino acid, peptide and protein produced by decomposed metamorphic and chemical hydrolysis. The second pollutant is coming from the chemicals used in the leather-making process, such as sodium sulfide, industrial salt, lime, chromium, dyes and all kinds of acids and oils, polymers, etc. Parts of these chemicals are toxic to the human body and organism, the other discharge with the wastewater is not biodegradable.

For the first category, it is mainly natural fats and protein-based. Because of good biodegradability and easy disposal, its negative impact to the environment is less. Therefore, it is not necessary to worry about the first category of pollutants.

In terms of source, pollution caused by leather production is mainly from the above mentioned second type of pollutants. Most of these substances, particularly sulfides, chromium, etc, have a direct poisoning effect on environment, human, animal and plant. For these discharge, their separation, collection and treatment are difficult. It is notable that, due to technical and cost constraints, there is no wider choice in the selection of leather chemicals raw materials. A considerable number of specialty leather chemicals, such as tanning agents, fatliquor etc, inevitably containing restricted or prohibited chemical composition which is legislated by the EU, are eventually brought into the leather products. Certainly, pollutants caused by the synthesis process of leather specialty chemicals, such as wastewater, waste gas, are also worthy of attention, especially the issue of wastewater and organic solvents.

The paper will focus on the leather specialty chemicals used during the wet finishing stage, such as organic tanning agents and fatliquor. For the synthesis of chemicals, green chemistry has recognized 12 principles to follow[1]. The so-called green chemistry is using the chemical principle to eliminate or reduce the use and generation of toxic and hazardous substances during the chemical design, manufacture and application[2]. Comparing with green chemistry 12 principles and combination of leather chemicals production process, we can initially determine some basic principles and directions of technological development for producing and processing environment-friendly specialty chemicals for leather.

1.1 Pollutant prevention

A considerable number of leather chemicals, such as sulfated oils fatliquor, will bring a large number of wastewater. Because of its high disposal cost and staining, products in this category will gradually be phased out if there would not be breakthrough in processing technology.

1.2 Using the low toxicity or non-toxic raw materials

The main problem of leather chemicals synthesis is to avoid using the organic solvents. The use of organic solvents not only causes pollution, but also significantly increases the cost, neither economic nor security. For example, in the phosphorylation oils and fats production process, the technology using organic solvent to disperse phosphorus pentoxide has been eliminated.

(3) Designing efficient chemical with low or little toxicity

During the tanning process, leather chemicals always go through the process of infiltration, combine and emission. It is hoped that the rate will have a substantial increase in infiltration and combination, lead to a significant reduction in emissions. This needs adequately consideration in the initial design of the synthesis. Additionally, in order to avoid those unwanted component eventually being taken into finished leather, it is necessary to be careful using some components and auxiliaries.

1.4 'Bio-degradable chemical

In leather processing, there are always remaining parts of chemicals which can not be absorbed by leather and discharged together with waste water or waste material finally. People hope that these substances could be degraded in a relatively short time with little or without harm to the environment.

2 Development tendency and several key techniques of environment-friendly leather chemicals

2.1 The main direction of development

Because the leather chemical industry lies in the first client of leather industry chain, advances in which will lead to remarkable progress in leather industry. Although China is weak in leather chemical industry, the good news is China's leather chemical enterprises and scientific research institutions have been increasing investment in research in recent years and achieved great progress. Be based on above four principles, we focus on following directions in producing green tanning agents and fatliquor.

(1) Developing biodegradable fatliquor. Biodegradable organic matter is one of concerned things. The main component of fatliquor is the organic matter with fatliquoring function and surface active agents for dispersed emulsion, which are difficult to be detraded in biological treatment process of wastewater. To the fatliquor, first of all, need to improve its absorption rate in using. Many small and medium-sized tanneries are still using sulfated or oxidation sulfited fatliquor. Although these two types of products have a certain characteristics in performance, during the production process they will discharge a large scale of wastewater and can be replaced by the others. We advocate to develop sulfur trioxide sulfonation, phosphorylation and sulfonation succinate combination fatliquor gradually to replace sulfated or oxidation sulfited fatliquor.

(2) Developing high-efficiency retanning fatliquor material. Combining retanning with fatliquoring is always the goal that the leather production has been pursuing, which not only can simplify the process but also save materials and reduce emissions. On abroad, there are already some mature products with superior properties. But in our country it is relatively backward in this area, and there is no corresponding products to sell in large-scale.

(3) To develop high-performance leather retanning filling material employing new technology. The traditional retanning filling material with linear molecular structure cannot satisfy need of leather performance increasingly enhaned. In order to break through the bottleneck, it is necessary to employ new technology to develop retanning filling material with novel structure. Hyperbranched polymer shows the attractive prospect. Our research results showed that retanning filling agents of hyperbranched polymer with a certain branching degree, molecular weight and distribution are obviously superior to the traditional mainstream market products in some performance. Especially, the selective filling and dyeing properties.

(4) amino resin tanning agent with low formaldehyde content. Amino resins have outstanding performance characteristics, however, the release of aldehydes after using is the issue that has always been difficult to solve. The only effective way is to reduce formaldehyde emissions using special technical measures to comply with the requirements of relevant standards.

2.2 Recommending several key technologies

During the development of environment-friendly chemicals for leather, there are a few basic skills that we are pleased to use and recommend. choosing non-toxic or low toxicity raw materials, using the

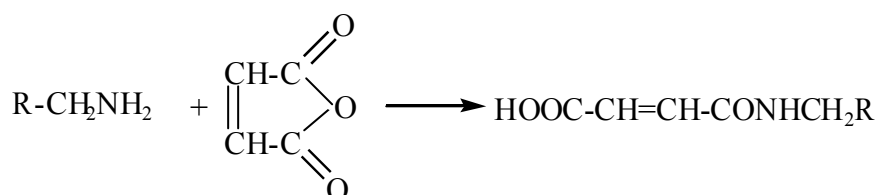
chemical reaction of high atom economy and avoid using organic solvents as far as possible, trying to achieve systematic greening of chemical synthesis process, application and after use.

2.2.1 Based on efficient esterification from maleic anhydride and alcohol to produce leather fatliquor materials

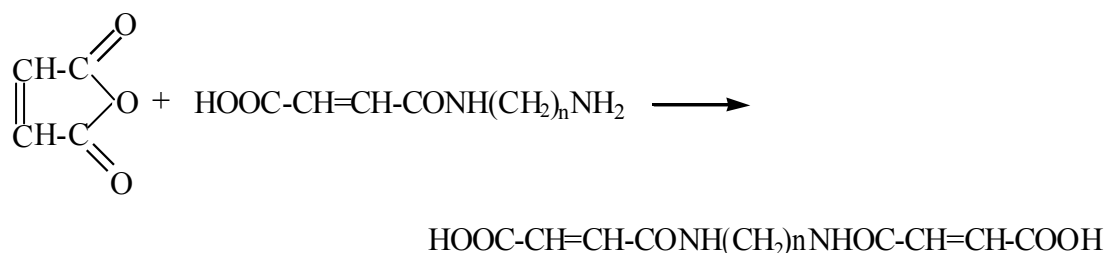
In leather chemicals synthesis, not maleic anhydride but its derivatives have often been used as a monomer in copolymerization producing retanning agent. The following are several typical reactions for preparing maleic anhydride derivatives:

(1) mono-amidation reaction using maleic anhydride with organic amine

In this reaction, maleic anhydride, as acylating agent, reacts with monamine or polyamine. Reacting with polyamine, maleic anhydride could be employed to prepare amphoteric derivatives with amino, which is intermediate product.

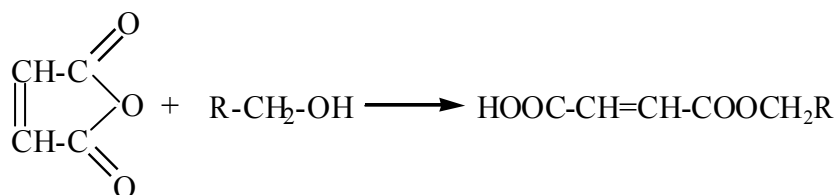


Of course, if the reaction above using the diamine, the monamide generated by the reaction can also continue to reaction with maleic anhydride, the reaction can be expressed as following:



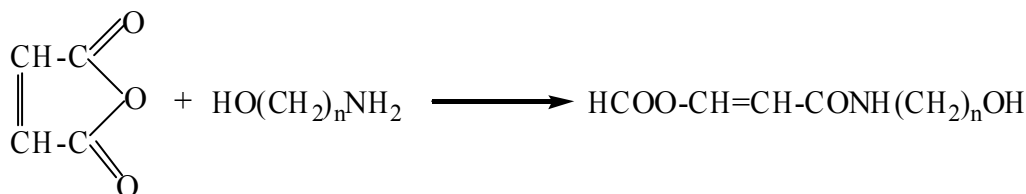
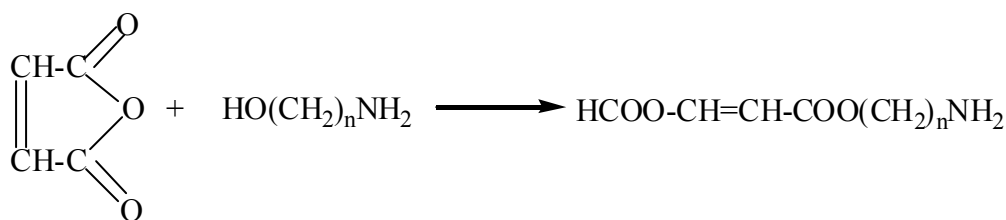
(2) Esterification from maleic anhydride with alcohol

Esterification using maleic anhydride and alcohol is easy to occur because of the positive charge of two carbonyls in the conjugate ring of maleic anhydride molecule, which enhances the activity of acylation.



(3) Amidation or esterification from maleic anhydride with alkylol amine

The reaction from maleic anhydride with alkylol amine is relatively complex. It occurs accompanying with many side reactions if using primary amine and secondary amine. However, side reaction rarely happens if using tertiary amine. Amidation and esterification reaction can be expressed respectively as follows:



In accordance with the requirements of target product, these two reactions not only can be simultaneously occur, but also happen dependently through the choice of reactants and control of the reaction conditions.

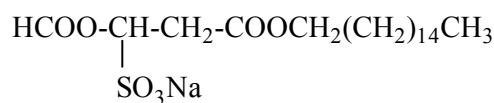
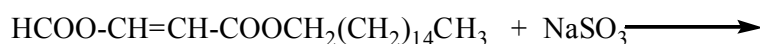
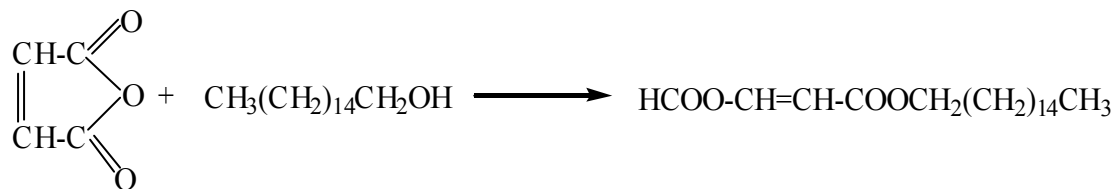
All the reactions from maleic anhydride with compounds containing active hydrogen above, are very useful in leather chemicals synthesis, particularly in retanning agent and fatliquor synthesis. After above reactions, the double bond of maleic anhydride is still there and can be used as monomer in copolymerization with vinyl monomers, such as methacrylic acid acrylic acid, acrylamide, acrylic acid ester etc, to get tanning agent with wanted properties.

2.2.2 Producing leather fatliquor materials using sulfonation succinic acidification reaction

After introducing the maleic anhydride unit into the molecular structure, sulfite is used to reduce the double bond accompanying with sulfonation, which not only can achieve succinic acidification, but also introduce the sulfonic group into molecular structure and improve the products' hydrophilicity. The typical reaction is as following:

(1) monoester of sulfosalicylic succinic acid and higher fatty alcohol

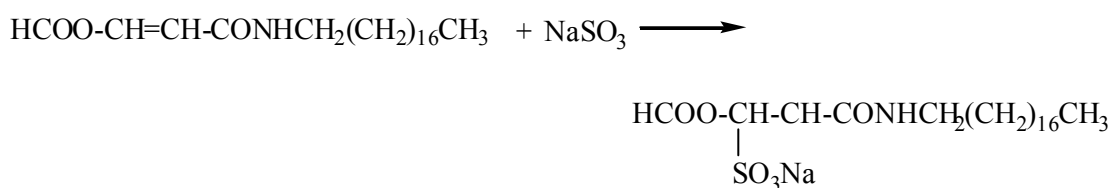
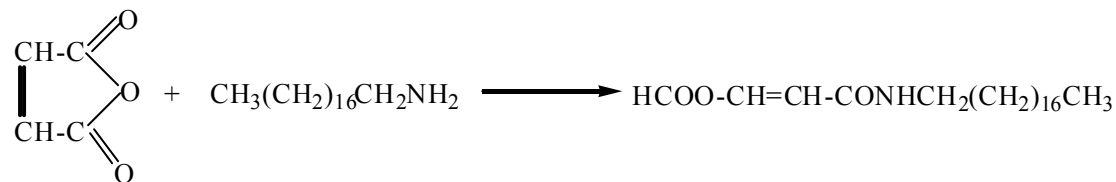
From maleic anhydride with higher fatty alcohol, such as dodecanol, cetyl alcohol, octadecyl alcohol etc, under no harsh conditions, higher fatty alcohol mono-maleate could be obtained. it then could be sulfonated using pyrosulfite or sulfite to prepare monoester of sulfosalicylic succinic acid and higher fatty alcohol. This product can be used as the main component to fatliquor leather. Using the cetyl alcohol as an example, the main chemical reaction as follow ing:



(2) sulfosalicylic succinic acid long -chain alkyl monamide

Long-chain alkyl mono-maleamide could be prepared employing maleic anhydride and saturated

long-chain fatty amine with C12-24. it is then sulfonated by pyrosulfite or sulfite and obtain sulfosalicylic succinic acid long-chain alkyl mono-amide. This product can be used as the main components to fatliquor leather. Using the octadecylamine as an example, the main chemical reaction as following:



2.2.3 Synthesis technology of branched retanning filling material

Most of the hyper-branched polymers were obtained by the way of gradually polymerization through condensation reaction with monomer AB_x. In order to speed up the reaction rate and have the satisfactory conversion rate, the small molecules produced by condensation reaction must be removed immediately. And unavoidable use of a large number of organic solvents not only pollutes the environment, but also is inconvenient to the process.

Because of advantages, such as simple, low cost and wide application, etc, the traditional method of radical chain polymerization is one of the most common methods used in industrial production of polymer. But in hyperbranched polymer production, this method is used very rare[3]. If it could be applied in hyperbranched polymer producing, the advantage is obviously: reaction can be carried out in aqueous solution, non-use of organic solvents; polymerization monomer is in large scale for choice; do not require complex separation process while reaction ended; and has advantages, such as technology feasible, low cost etc, in large-scale production, etc.

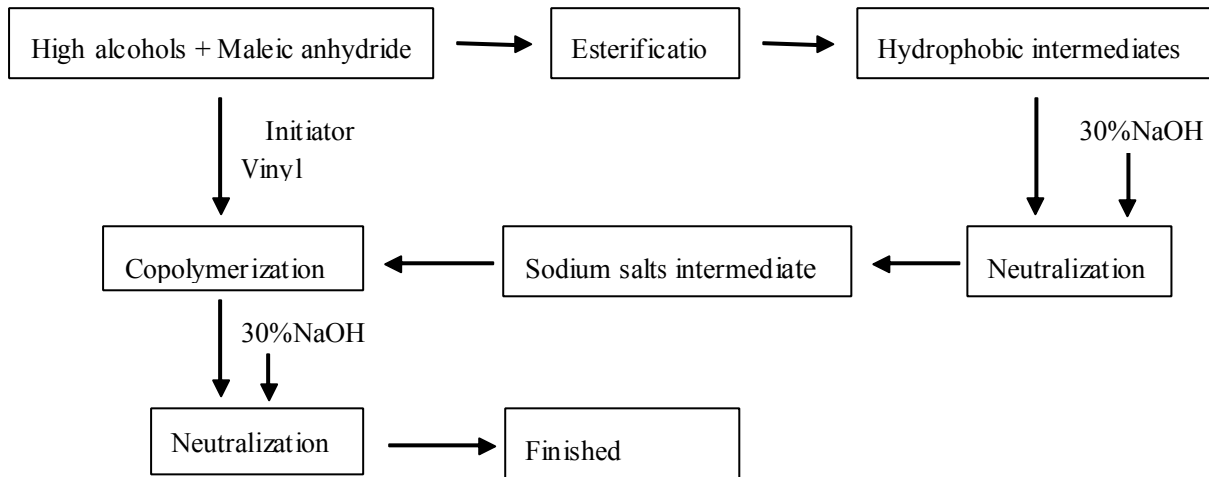
The main disadvantage of this method is the degree of polymerization and degree of branching are more difficult to control, and the molecular weight of the products has a wide distribution. However, natural leather, mainly about animal skins as the raw materials, has the unique micro-structures. Because of quality of its internal collagen fiber, such as thickness, length, texture and weave angle and the degree of weaving, has great difference in the different parts of the body. That requires the retanning filling materials has a wide distribution of molecular weight, in order to satisfy the filling requirements of the different parts of raw leather. The molecular weight of the hyper-branched polymer, which Synthesizing through the way of radical chain polymerization, has a wide distribution. And it has the possibility to satisfy these requirements.

3 Introducing the typical environment-friendly leather chemicals produced by Brother Enterprises Co., Ltd

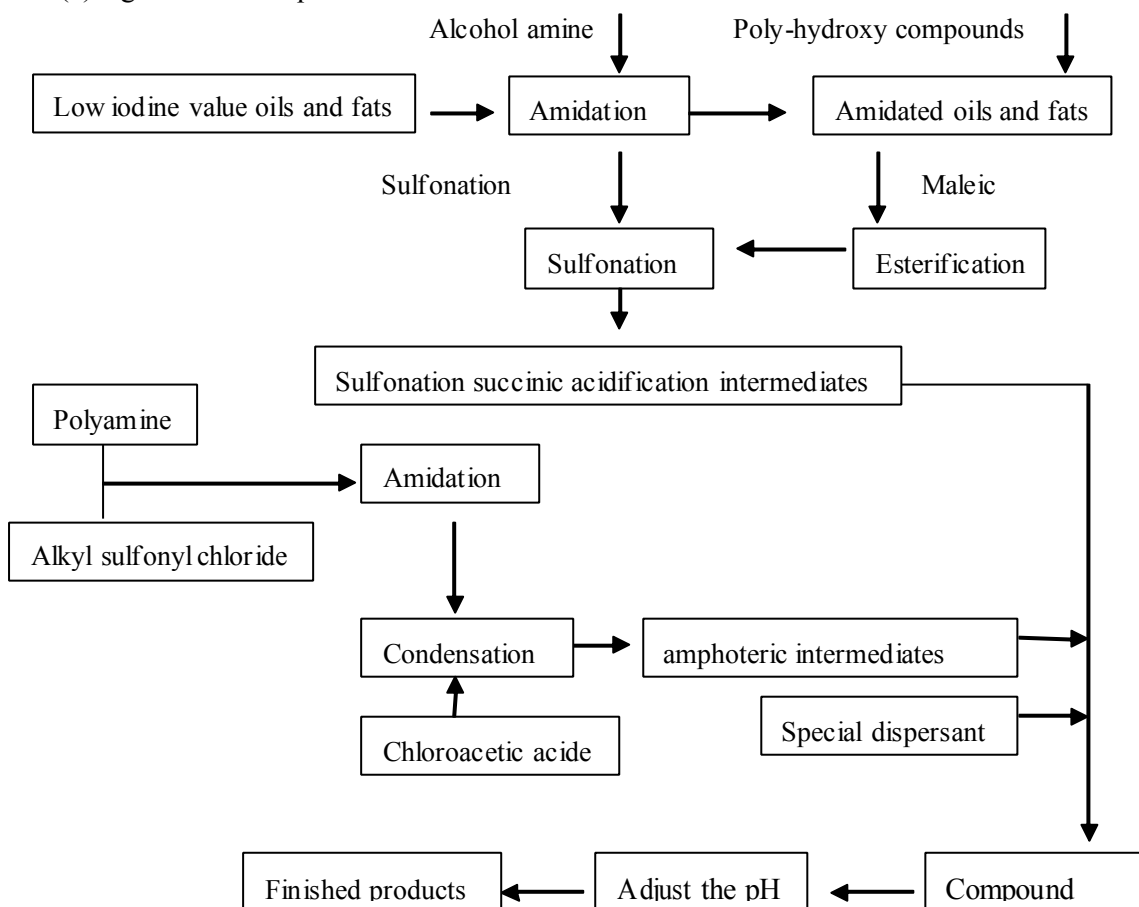
Recent years, Brother Enterprises Co., Ltd., as a chemical enterprise is in the leadership of leather chemical industry in the scale and technology, always cooperates with the high-level scientific research institutions in domestic. And it has been working in high-performance environment-friendly leather

chemicals' research, development, production and sale. And some products have been made large progress in the level of the green and application performance.

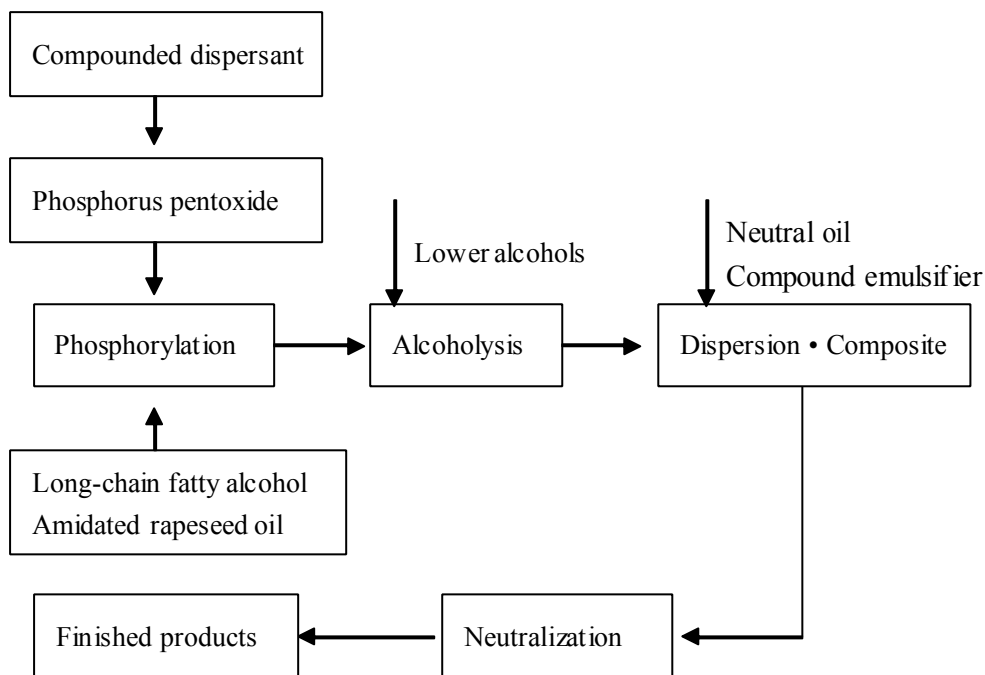
(1) The synthetic route of functional polymer fatliquor BRPOLY-RF is as follows



(2) high-bound fatliquor



(3) The synthetic route of fatliquor phosphate BROSOL-BP is shown below:



4 Introducing the Brother Enterprises Co., Ltd.'s typical applied clean technology

(1) Cleaning and high-absorption chrome tanning technology: it is a chrome tanning method with non-pickling, high absorption and low chromium. In the end of chrome tanning, chromium sesquioxide in the waste-liquid can be controlled in the 200mg / l or less, no sodium chloride emissions.

Normal softening the leathers; use a synthetic acid phenols material pre-tanning agent BROTAN-NTS(2-5% in 100%), to deal with it in 30 °C bath for 2 hours, then 1.0-1.5% chromium tanning agent BROTAN-BHN($\text{Cr}_2\text{O}_3\%$ =9-11%) treat for 2 hours, finally take process of squeezing water, tablets skin, shaving; use 1.5-2.0% polymer tanning agent BRPOLY-SMP, which contain free active groups and polymer dispersion component, to deal with 40-60 minutes; add 3% chromium powder HLS-C ($\text{Cr}_2\text{O}_3\%$ = 25%, $\text{b}\%$ = 33%) to deal with 2-3 hours; add 0.5% chrome tanning auxiliaries agent HR to deal with 1-2 hours, using magnesium oxide extracted alkali 6-8 hours (temperature 39-40 °C, pH4.0, TS > 102 °C).

Pre-tanning agent NTS, polymer tanning agents SMP, as well as chrome tanning auxiliaries agent HR are environment-friendly green leather chemicals.

(2) The applied technology of hexavalent chromium prevention

In the premise of avoid excessively high value pH (controlled with the use of sodium bicarbonate), using a new neutralization tanning agent BROTAN-PN, which containing antioxidant components, and has the both capability of reducibility and tanning, to neutralize in the process of wet-blue leather and extracted alkali during the latter stager of chrome tanning, not only can effectively prevent generating hexavalent chromium, but also be significantly improving the level dyeing of leathers and the uniform distribution of tanning agent and fatliquor in latter stage, finally improve the quality of leather.

(3) The applied technology of formaldehyde-free retanning

In modern leather industry large-scale use of phenolic and amino resins synthetic tanning agent is utilized or synthesized by formaldehyde, would release formaldehyde in the process of using, lead the

leather containing formaldehyde or even exceeded. Using Brother Enterprises Co., Ltd.'s tanning agent, which does not contain formaldehyde and produced with the new condensation technology and special molecular structure design, such as BROTAN-NFR, BROTAN-CPR, BROTAN-FI, etc, would not be formaldehyde release in the process of using, and the quality of the leather has better softness and dyeing properties compared to the traditional formaldehyde condensation tanning agent, even can improve the light resistance

(4) The applied technology of chromium-free tanning technology

First use pre-tanning agent BROTAN-NTS(3-5% in 100%) to treat it in 30 °C bath for 2 hours, after adjusting pH value by formic acid, to deal with it for 2-3 hours using 5%zirconium tanning agent, then overnight inter-turn. Use 2-3% naphthalene - aluminum tanning agent to deal wit 2-3 hours next day, extracted alkali to 3.5-3.7,wet-white leather shrinkage temperature up to above 95 °C , then take process of squeezing water, tablets skin, shaving. Use fatliquor BROSOL to fatliquoring and new deep- fixing agent BROFIX to improve problem of wet-white leather dyeing. Yield of leather, Physical and mechanical properties, and style of finished leather is close to Chrome-tanned leather

Explanation : BROTAN, BRPOLY, BROFIX and BROSOL are the Brand of Brother Enterprises Co., Ltd.

5 Recommendations and outlook

On the international market, the requirements to the leather products are increasing tendency to focus on problem of Ecological and health.

The corresponding standards and instruction formulated by countries and regions, Represented by the EU, is becoming increasingly strict and harsh. Despite the non-discriminatory, but in fact this is a great obstacle to most of the enterprises of China's export trade. We can not continue to hover at a low level, from the view of our own point, and should actively take the initiative to enhance the innovative ability to develop more adequate technical content, a higher grade, more value-added products is the only way out. In this very difficult elevating process, domestic leather chemical industry, as the raw material provider and the upstream industry of the leather industry, must be forward-looking research and development, in order to Offer a richer, higher level of green, high performance chemicals for Leather enterprises. We believe that it should be strengthen the research on the following aspects in the future

First, develop non-chrome tanning agent and its applied technology.

Due to the shortage of chromium resources and people's inmost sensitivity bring by recognized toxic of chromium, the non-chrome tanning products will be greatly required in the future. Standard of national and enterprise, like japan and adidas, nike, etc, not only limit content of hexavalent chromium in leather, but aslo limits content of total chromium.

At present, the state environmental protection department is also actively formulating the requirements of environmental labels on leather products and technical, inside the draft is clearly limit the content of hexavalent chromium and total chromium

Second, invent high absorption, high-fixed, high-performance and easily biodegradable fatliquor and tanning agent and its applied technology. The requirements of reducing emissions of chemicals in leather producing are continuously rising. It is not only solve from technology, but more importantly, the absorption rate, fixed rate, performance and other issues as well as the degradation rate should be take into account from the beginning of design and chemical synthesis

Third, replace or eliminate the harmful components of leather chemicals.

It is mainly directed against substance of alkylphenol polyoxyethylene ethers, which bring by emulsifier and related raw materials. Because of high toxicity to animals and plants, the EU's requires limited using four categories of these

Fourth, the active use of new technologies to develop new materials for leather chemicals, to break limitations of traditional leather chemicals

The hyperbranched synthesis technology has been proven have broad application prospects in the leather chemicals synthesis and application. Because of the difference in molecular structure, it has many advantages mainly comparing to the materials of linear-molecular structure. Particularly, in the choice of filling, dyeing properties, fixed-rate, etc, achieve a new level, and worth of depth study.

Fifth, actively research and develop of cleaner leather producing technology and green leather chemical's applied technology. Promote the market transformation of the leather industry clean results.

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