Improvement of Rosin Sizing Agent and Introduction of FCN Approved "FA Series”

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1. Introduction

SEIKO PMC is dedicating to providing high-quality specialty chemicals, development of environmentally-friendly materials, saving resources, and promotion of recycling to contribute to the creation of a sustainable society with the administrative vision “Explore the Future through Eco-Friendly Technology[1)]”. Specifically in our paper-making chemicals business, we provide paper-making chemicals and develop paper-making procedures to effectively use the chemicals that give unique functions to paper, allow the papermaking companies to use regenerated paper, reduce the consumption of water and energy that accompanies manufacturing of paper, and alleviate the effluent load.

In 2015, Sustainable Development Goals (SDGs)[2)] adopted by the United Nations include goals to conserve the environment, and paper that is made from cellulose, a recyclable resource, became a promising material, which in turn makes the paper-making chemicals and technologies increasingly crucial. Among the paper-making chemicals, “**sizing agent**” controls the degree of penetration of liquid through paper (size effect); and therefore, is an indispensable chemical to allow paper to replace plastic to make packages or containers.

Rosin-based sizing agent that uses rosin obtained from the sap of *Pinaceae* trees as the main ingredient has been used for ages, and its value is being reconsidered as a recyclable biomass material.

We became a pioneer in the development of the rosin emulsion sizing agent utilizing synthetic polymer emulsifier and have been improving the performance of the sizing agent by making better use of rosin. The rosin emulsion sizing agents commonly used nowadays are based on the technology to process rosin to maximize the size effect, the synthetic technology to prepare polymer that works as the emulsifier, and the emulsifying technology. We possess these technologies and apply them in various fields.

The first part of this technical review covers general functions and roles of rosin sizing agents. The following section reports our knowledge obtained through the development of rosin emulsion sizing agent. Lastly, the features of the new FCN-approved (Food Contact Notification) rosin sizing agents “FA series” developed based on the cumulative wisdom are introduced.

2. Sizing agent

Sizing agent is a group of chemicals that imparts the size effect to paper. The size effect is a phenomenon that increases the resistance of paper to water (i.e., the speed of penetration is reduced).

Desirable speed of penetration of liquid through a sheet of paper varies depending on what the paper is used for. Therefore, the role of sizing agent is to adjust the speed of penetration in a proper range. Figure 1 shows an example of how addition of sizing agent to the pulp prevents ink bleed on the paper by controlling the speed of penetration of the ink through the paper.

Figure 1. Comparison of water-based pen bleeding

The size effect is achieved by the hydrophilic moiety of the sizing agent being attracted to the surface of cellulose and the hydrophobic moiety being oriented away from the cellulose to increase the contact angle between a sheet of cellulose and liquid (Figure 2).

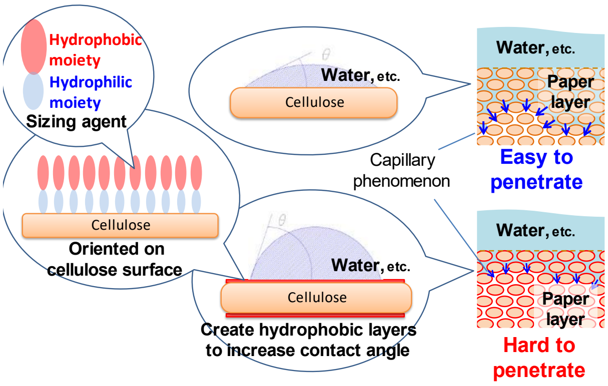

Figure 2. Principles of size effect

For this reason, the design of sizing agents should include a moiety that interacts with cellulose and one that increases the contact angle. Figure 3 shows the structures of the representative sizing agents. The common features of the chemicals are that they have large hydrophobic moieties and a hydrophilic moiety that interacts with cellulose.

Although how exactly the sizing agents interact with cellulose is under discussion it is at least known that alum (aluminum sulfate) is necessary for rosin sizing agent to express the size effect. Therefore, it is thought that the formation of salt between a rosin and an aluminum ion (Al^{3+}) could align the rosin molecule along cellulosic fibers (Figure 4)[3].

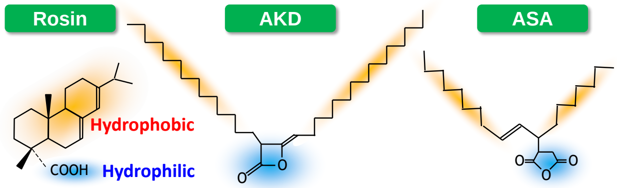

Figure 3. Structures of representative sizing agents

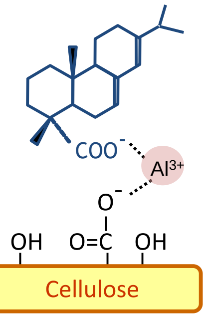

Figure 4. Interaction between a rosin sizing agent and cellulose

Because sizing agent components are highly hydrophobic as a whole and reluctant to mix with water, various efforts have been made to allow them to interact with the hydrophilic cellulose surface. Emulsion sizing agents widely used today overcome the solubility problem by allowing the sizing agent to disperse in water in a form of emulsion (Figure 5).

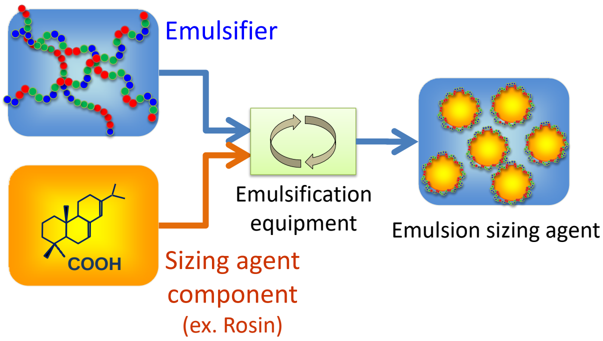

Figure 5. Emulsion sizing agent

The size effect is achieved in three steps (figure 6): 1) adsorption of the sizing agent to cellulose in water 2) melting of the sizing agent to spread over the surface of cellulose 3) interaction of the molten agent with the cellulose surface to render it hydrophobic[4].

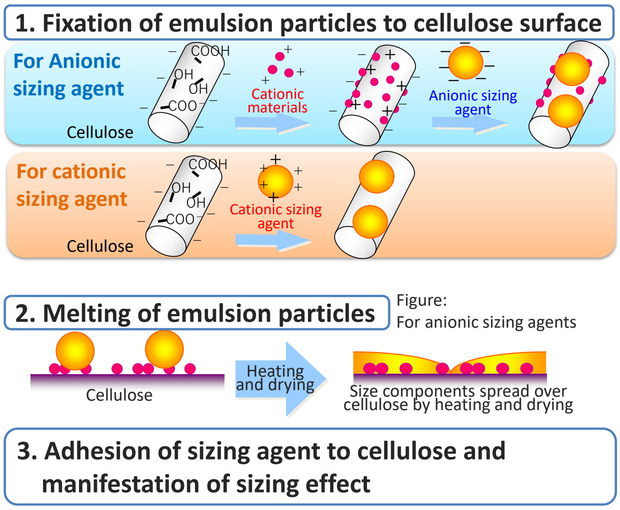

Figure 6 Mechanism of size effect by the emulsion sizing agent

The sizing agent has been designed so that size effect can be automatically expressed through the paper-making processes such as preparation of pulp slurry, preparation of wet paper on the open mesh and the presses, drying in the drier part, and coating on the size press and after-bank dryer.

3. Rosin emulsion sizing agent

Rosin has long been used as a sizing agent, but in the form of the alkali salt of rosin (rosin soap) called “solution rosin sizing agent (rosin soap sizing agent)”. The solution rosin sizing agent is added to pulp slurry and then mixed with alum (aluminum sulfate) to express the size effect. The mechanism is that after the rosin-aluminum salt (aluminum rosinate) is formed in the slurry and fixed to the cellulose, the hydrophobic moiety of the rosin is oriented during the drying process[5].

However, the formation of rosin-aluminum salt is dramatically affected by the pH of the paper-making water and the foreign substances in it. Therefore, the applicable pH is limited to around pH 4 to 4.5[6]. The rosin emulsion sizing agent often forms insoluble salt to spoil the paper as well.

In the 1930s, rosin emulsion sizing agents that were less susceptible to the operating conditions were developed for the first time by emulsifying the rosin with a small amount of alkaline base[7]. Unlike the solution rosin sizing agents, rosin emulsion sizing agents are less susceptible to the condition of water because the rosin-aluminum salt is formed on the cellulose surface during the drying process rather than in the pulp slurry. The rosin emulsion sizing agent was further improved by mixing with natural polymers such as casein as stabilizers[8]. In the 1970s, the rosin emulsion sizing agents containing low-molecular-weight surfactant came into use, but they were inferior to the solution rosin sizing agents in terms of the handling, which made them less popular. In the 1980s, we discovered that synthetic polymer-type emulsifiers were superior in stabilizing the emulsion and controlling the properties of the emulsion to the low molecular weight types. Therefore, we decided to market rosin emulsion sizing agents that use synthetic polymer-type emulsifiers[9].

Compared to the AKD and ASA sizing agents, emulsified rosin sizing agent can be stored at room temperature, does not require special addition facility, and is applicable to a weakly acidic to neutral pH range. For these reasons, the emulsion rosin sizing agent is commonly used in Japan. The next section briefly describes important technical advances in developing a rosin emulsion sizing agent at our company.

4. Improvement of emulsifying equipment and emulsifier

Rosin is solid at room temperature, and various methods have been proposed to emulsify it. In particular, it has the specific gravity greater than 1 and is prone to settling and separation. Therefore, it is necessary to increase the specific surface area and the electrostatic repulsive force at the interface between the emulsion particles to maintain the dispersion state by homogenizing it.

Currently, a typical preparation of rosin emulsion consists of liquification and emulsification using an emulsifier as other oily substances are emulsified. There are two main methods for liquefying rosin: the solvent method, in which solvent is used to liquefy the rosin, and the solventless method, in which rosin is heated to melt it. The solventless method is generally preferred because the solvent use will leave some residual solvent in the emulsion even after distilling it, which may be harmful to the environment and human.

Emulsifiers for rosin emulsions are generally anionic in Japan. One reason is that the dissociation of the acid in the rosin makes it more anionic in water during the paper-making process, whereas if cationic emulsifier were used, the charge of the emulsion would be neutralized to destabilize it.

Synthetic polymer-type emulsifiers, currently used, do not only contribute to the formation of emulsion during the emulsification step, but also remain on the surface of the emulsion after the emulsification to control the stability and the behavior of the emulsion in pulp slurry. The functions can be adjusted by the monomer composition (the amount and type), molecular weight, and distribution of hydrophobic and ionic groups in the polymer. Therefore, we have improved emulsification equipment, the composition of the emulsifiers, and others to develop an improved rosin emulsion sizing agent that (1) is readily adsorbed to cellulose in aqueous media, (2) melts and spreads by heat, and (3) makes the cellulose surface hydrophobic more efficiently through effective interaction with cellulose.

Figure 7 shows a comparison of Cobb size tests (a value representing the amount of water absorbed per unit area in a given time) for the products. The improved product only requires 20% less dosage than the conventional product to attain the same level of Cobb water absorption, indicating an enhanced size effect. The success in the development of the improved product was largely due to the enhanced power of the emulsifying machine, which allowed us to prioritize the performance of the resulting emulsion over the ease of making emulsion in the design of the polymer-type emulsifier.

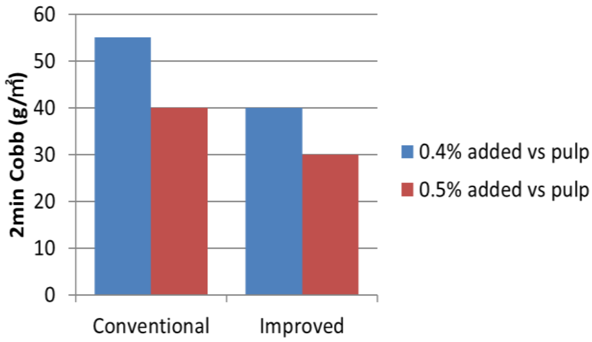

Figure 7. Sizing performance of improved product compared to the old one

Paper-making conditions:
pulp type : reused cardboard pH6.5、30°C、basis weight 80g/m^2
chemical : alum 1%→PAM (0.1%)→sizing agent

It was discovered that the use of the improved emulsifier also enhanced the stability of the emulsion in hard water. Hard water usually contains multivalent metal ions such as Ca^{2+} and Mg^{2+} that neutralize the charges on the carboxyl groups on the surface of the anionic emulsion to precipitate or coagulate the emulsion, which results in dirt formation or deterioration of the sizing performance. Figure 8 shows microscopic images of the diluted emulsion in hard water with electrolyte concentration of 3000ppm, which shows that the improved product produces much less coagulants. Paper-making machines in recent years reuse water, but the water is hardened as it is used repeatedly. The coagulation of emulsion is suppressed even under such paper-making conditions, which helps the sizing agent evenly distribute themselves onto cellulose to efficiently achieve the size effect as well as reduce the dirt formation.

Figure 8. A comparison of images showing the degree of coagulation when conventional and improved product are diluted

5. Development of the component that contributes to size effect

"Fortified Rosin" that is formed by adding a conjugated carboxylic acid such as fumaric acid or maleic acid to the diene in a rosin molecule by Diels-Alder reaction (Figure 9) is known to exhibit a superior size effect. The difference is attributed to the extra carboxyl groups that also interact with cellulose via aluminum (Figure 10).

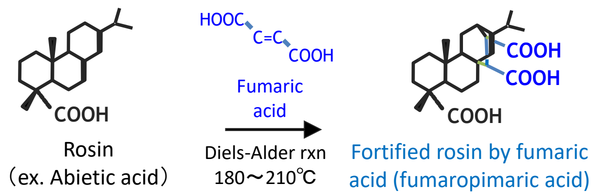

Figure 9. Synthesis of fortified rosin

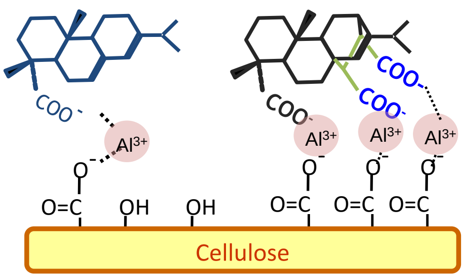

Figure 10. Mechanism of how fortified rosin shows an improved size effect

As shown in Figure 11, rosin and fortified rosin dissolve in water as a result of gradual dissociation of the acid in the process that we call "elution", which causes reduced sizing performance and bubbles by the formation of soap. Therefore, conventional rosin sizing agents that use rosin or fortified rosin alone were not suitable for high pH conditions where dissociation of acid is facilitated.

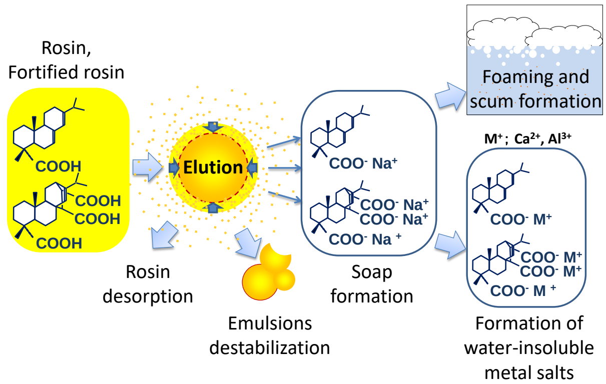

Figure 11. Problems caused by "elution" of rosin

This problem had been tackled by companies including us in Japan, and the rosin sizing agents that are resistant to the elution under weakly-acidic to neutral conditions are sold. Such sizing agents are prepared by mixing the rosin ester, obtained by reacting rosin with polyol, and the fortified rosin (Figure 12), which allows the mixture to maintain the decent levels of size effect in high pH conditions suitable for AKD and ASA (Figure 13). Therefore, in Japan, it is often used as a countermeasure for various problems associated with ASA and AKD sizing agents (ASA-derived stains, AKD-derived slippage, and low cure rate).

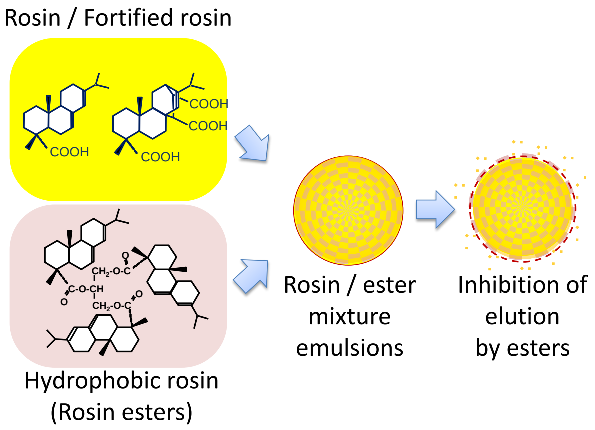

Figure 12. Suppression of elution by adding rosin ester

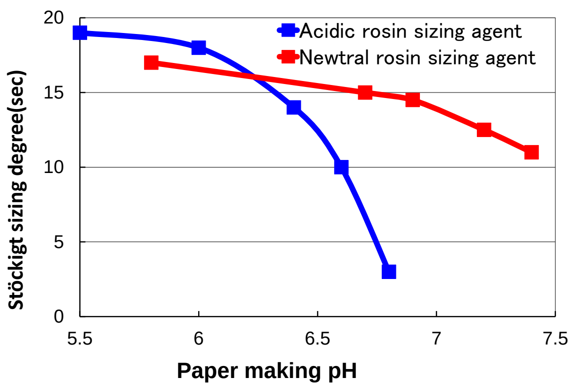

Figure 13. Comparison of the performance of acid and neural rosin sizing agent at different pH

Paper-making conditions:
pulp type: BKP, basis weight 70g/m^2
chemical: alum1.5%→sizing agent 0.3%→retention aid0.01%

Although the elution mechanism has not been fully elucidated, reducing the exposure of the carboxyl groups on the surface of the emulsion or the hydrophobic interaction between rosin and rosin ester could keep the rosin from leaving the emulsion.

6. Optimization for paper-making machine

Once rosin emulsion sizing agent is adsorbed on cellulose in the wet end process, the wet paper is pressed and dried to be dehydrated at a fast rate at a very high temperature. During these processes, the rosin emulsion particles in the paper are molten and interact with cellulose via aluminum ion to orient themselves so that the hydrophobic moiety is exposed outside to achieve the size effect.

Thus, how easily rosin melts to thinly spread on the cellulose surface is an important factor for rosin molecules to effectively interact with aluminum ions and cellulose. In general, fortified rosin is used because an excellent size effect is expected (Figure 10) by increasing the number of aluminum-mediated interaction with cellulose. At the same time, however, fortified rosin makes strong intermolecular hydrogen bonds. The more fortified rosin in the sizing agent, the more difficult it is to thermally melt it, and the less size effect that is developed under the same drying conditions. Hence, the benefit and drawback are in a trade-off relationship, and it is important to adjust the fraction of the fortified rosin according to the paper-machine and paper-making conditions in which the sizing agent is used. We find the best composition of the rosin sizing agent by investigating customers’ paper-making conditions and testing the samples under the reproduced conditions in our lab.

7. “FA series”, FCN-approved rosin sizing agent

Recently, paper is regarded as a promising material to replace plastic from the perspective of the SDGs. Sizing agent, especially, is expected to be used in paper that may come into contact with food because the sizing agent plays an important role in controlling the penetration of liquid through paper. Therefore, the sizing agent is required to be extremely safe .

In prospect of such a business trend, we introduced “FA series”, the alternative to AL and CC series sizing agents (see Table 1), which is the FCN (the Food Contact Notification) approved by the FDA (U.S. Food and Drug Administration), to the market.
Furthermore, the dosage of FA series can be as high as

an FCN-approved maximum addition ratio of approximately 3% versus paper weight, which is about 10 times higher than that of ordinary paper and paperboard, making it suitable for applications requiring stronger water resistance performance.

Table 1. New rosin sizing agent “FA series”

	FA1140 Series Acidic	FA1160 Series Slight-acidic	FA1170 Series Neutral
Applicable pH	4.0～5.5	5.5～6.5	6.5～8.0
Corresponding conventional products	AL1200 Series	AL1300 Series	CC1400 Series
Total solids(%)	50	50	50
Viscosity(mPa・s)	<100	<100	<100
pH	Approx.5～7	Approx.5～7	Approx.4～6
Note	FCN（U.S.）approved, Chemi-net（Japan）listing BfR（Germany）・GB（China）application in process		

We are currently preparing applications for BfR Recommendation XXXVI (Germany) and GB9685 (China) for these products.

8. Oversea activity

Figure 14. SEIKO PMC VIETNAM Co., Ltd.

The construction of a new factory in Vietnam had been completed, and it is now operating (Figure 14). We are preparing to sell the abovementioned “FA series” as well as other products in Southeast Asia.

9. Conclusion

Rosin sizing agent, especially rosin emulsion sizing agent, is a biomass derived product that has been used for a long time by many users for making various types of papers under different paper-making conditions. The rosin emulsion sizing agent and the relevant technology are expected to be increasingly important in the future.

We continue to improve our rosin emulsion sizing agent and apply the knowledge obtained from the experience to other products to realize the sustainable society.

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