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The Recent Tendency of Environmentally-friendly Tackifiers

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It is a main trend not to use organic solvents in the adhesive industry from the recent environmental and safe points of view. For example, water-based, hot-melt, or UV curable adhesives are being investigated. Several different kinds of tackifiers that are formulated in the adhesives in order to give them more functional properties like initial tack and higher adhesion, etc., have been proposed to meet the recent trend. Firstly, the characteristics and fundamental properties of the respective materials are presented. In Japan, the trend to develop the water-based adhesives is most remarkable. While the environmental regulations are getting harder, Arakawa Chemical has been spending a lot of energy for the research, and developed toluene-free and solvent free tackifier dispersions that are presented precisely.

1. Introduction

In the adhesive industry, solvent-based adhesives have being replaced by water-based, hot-melt, or UV curable adhesives from the recent environmental, workers' health and safety points of view. In the field of adhesives, for example floor adhesives, much development of the water-based adhesives have been performed using polymer dispersions like chloroprene latexes, urethane dispersions, acrylic polymer dispersions, ethylene-vinyl acetate copolymer dispersions and so on. Conventionally, the water-based adhesives had many technical problems like poor adhesion, slow drying in comparison with the solvent-based adhesives. However, by improvement of the formulation technology such as the addition of tackifiers, the movement from solvent-based to water-based is particularly active.

In the field of pressure sensitive adhesives (PSAs), this tendency is conspicuously seen as shown in Figure 1 [1]. PSAs formulated with the acrylic polymer dispersions have been used in almost all of the labels made with paper substrates aside from film substrates in which higher water resistance is necessary.

In such the tendency, Arakawa Chemical has recently developed the tackifier dispersions for the water-based adhesives in order to promote the shift to the water system. As adhesive makers have investigated the addition of our tackifier dispersions to the adhesives in the above field, their requirements for the performance of tackifier dispersions have changed to higher and wider levels. There are new problems in the field of building and automobile-related materials; it is "indoor air quality" pro-

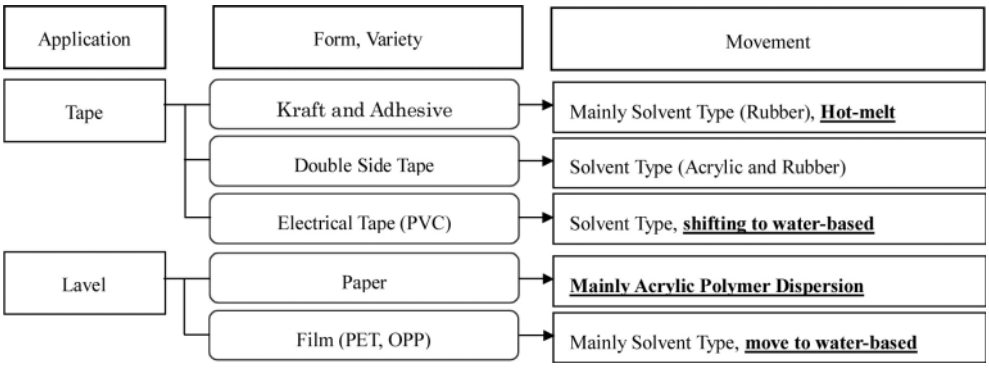

Figure 1. Market movement in Japan.

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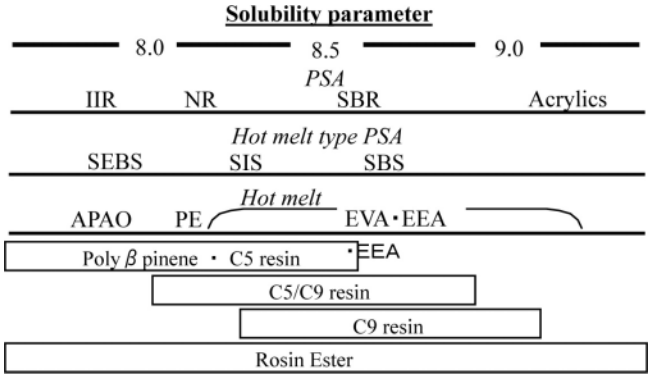

Figure 2. Compatibility and solubility characteristics of several tackifiers.

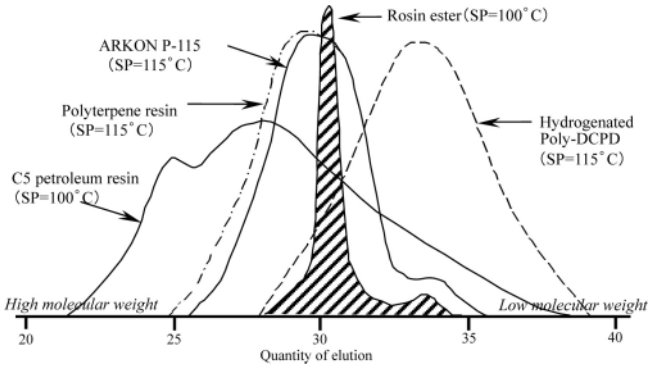

Figure 3. Molecular weight distributions of several tackifiers (GPC).

blems.

In order to be proposed to meet the trend, Arakawa Chemical investigated the emulsifiers, preservatives and the emulsification methods, and developed two types of new environmentally-friendly tackifier dispersions; toluene-free type "SUPER ESTER NT" series and solvent free type "SUPER ESTER NS" series. In this presentation, we reported the generalization about the tackifier dispersions and the trend of the correspondence for recent environmental problems in the adhesives industry.

2. Tackifier Dispersion

The tackifier dispersion is an oil in water (O/W) emulsion, in which the tackifier is dispersed in water with the emulsifiers. The tackifier is an amorphous oligomer, and it is added in base polymer system like acrylic polymers or rubbers in order to improve the properties of the adhesives.

There are various kinds of tackifier resins such as rosin derivatives, terpene resins, C-5 or C-9 hydrocarbon resins, and phenolic resins. When choosing the tackifier to modify the adhesives, there are two important characteristics to be considered; the compatibility and glass transition temperature (T_g) [2]. The compatibility is influenced by the solubility parameter, molecular weight and molecular weight distribution of the tackifier resins. Among several tackifier resins, the rosin derivatives show better compatibilities for many kinds of the base polymers due to its wide solubility parameter and narrow molecular weight distribution, so these have been used widely in many fields of adhesives.

3. Resin Emulsification Technology

In the resin emulsification, two types of emulsification methods are generally well known. One of them is the phase-inversion emulsification, which is a chemical method using the emulsification power of the emulsifier effectively. The other is the mechanical emulsification, which is a physical method using the mechanical power such as high pressure.

Two methods have their own characteristics shown in Table 1. In the phase-inversion method, the production equipment and process are generally simple, but the choice of emulsifier is very difficult and a high amount of emulsifier is necessary. On the other hand in the mechanical method, the exclusive and expensive equipment is necessary and the process is complicated. At the point of emulsifier, a small amount of emulsifier is required for the emulsification and emulsifier can be chosen widely. The kind and amount of emulsifier remarkably affect the performance of the adhesives like the compatibility to the base polymer, adhesion and water resistance, and therefore, the mechanical emulsification method has been mainly used to obtain the tackifier dispersions in Arakawa Chemical as shown in Table 2.

4. Recent Correspondence for Environmental Problems

The adhesives are requested to be much more environmentally-friendly in these days. In particular, "endocrine disruptors" and "indoor air quality" problems are current concerned issues in the Japanese adhesive industry.

Table 1. The characteristics of emulsification methods

	Mechanical emulsification	Phase-inversion emulsification
Equipment	Exclusive and expensive	Simple
Safty	Attention fod solvent use	Basically safe
Process	Distillation is necessary	Only emulsification process (Distillation is unnecessary)
Emulsifier	Low amount Wide choice	High amoun Choice is limited and difficult
Particle size	Small, narrow distribution	Large, wide distribution

Table 2. Typical properties of conventional tackifier emulsions

Item \ Products	Super ester				Tamanol	
	E-720	E-730-55	E-650	E-865	E-100	E-200
Solid content (%)	50～51	55～56	50～51	50～51	52～54	52～54
pH	5～7	5～7	5～8	6～9	6～8	6～10
Viscosity (mPa・s)	<200	<200	<200	<1000	<200	<220
Particle size (μm)	0.4～0.7	0.4～0.7	0.4～0.7	0.4～0.7	0.4～0.7	0.4～0.7
SP of resin (^{o}C)	Anionic	Anionic	Anionic	Anionic	Anionic	Anionic
Kind of resin	Ester of stabilized rosin		Ester of stabilized rosin		Rosin phiolic	

Table 3. Guideline values for indoor air concentrations

VOCs	Formaldehyde	Toluene	Xylene	TVOC
Guideline value for indoor air concentration	100 μg/m^3 (0.08 ppm)	260 μg/m^3 (0.07 ppm)	870 μg/m^3 (0.20 ppm)	400 μg/m^3

There was a case that the tackifier dispersions have included a small amount of the materials causing these problems till now. Therefore, the removal of those materials was expected strongly. A general tendency and our actions to solve the problems are as follows;

4.1. Nonyl/octyl Phenol

To obtain the tackifier dispersions, the use of the emulsifier is absolutely necessary. Because emulsifiers of nonyl/octyl phenol ethoxylate type are superior in emulsification ability and cost, these had been used to emulsify the tackifier resins widely for many years. However, it was suspected that nonyl/octyl phenol, which was the raw material of the emulsifiers, was an endocrine disruptor.

Because emulsifiers in tackifier dispersions affect the mixing stability with the base polymer dispersions and the adhesive performance, the choice of them must be carried out carefully. As a result of trials, it was found out that a specific non-nonyl/octyl phenol type emulsifier had excellent emulsification ability for tackifier resins and wide mixing stability for the many kinds of base polymer dispersions, and therefore, emulsifiers were already substituted to nonyl/octyl phenol ethoxylate type in all of our products.

4.2. Formaldehyde

The tackifier dispersions, especially consisting of natural source resins like a rosin ester, have a fundamental putrefactive problem. To prevent putrefaction, formaldehyde had been added in the emulsions widely due to high preservative ability and low cost. However, “Ministry of Land, Infrastructure and Transport” in Japan indicated the guideline value for indoor air concentration of formaldehyde (shown in Table 3), and it obliged tackifier dispersion makers not to use formaldehyde. To

Table 4. Typical properties of environmental-friendly tackifier emulsions

Item \ Products	Super ester		Tamanol	Super ester			
	E-625-NT	E-865-NT	E-200-NT	NS-100H	NS-125A	NS-100A	NS-120B
N.V (%)	50～51	50～51	52～54	50～51	50～51	50～51	50～51
pH	6～9	5～8	4～8	6～9	5～8	4～8	5～8
Viscosity (mPa・s)	<200	<300	<300	<200	<200	<200	<200
Particle size (μm)	<0.6	<0.6	<0.6	<0.3	<0.3	<0.3	<0.3
Ionic	Anionic	Anionic	Anionic	Anionic	Anionic	Anionic	Anionic
SP of resin (°C)	125	160	150	100	125	100	120
Kind of resin	Ester of polymerized rosin		Rosin phiolic	Ester of stabilized rosin		Ester of rosin acid modified rosin	
Characteristics	Toluene free			Solvent free			

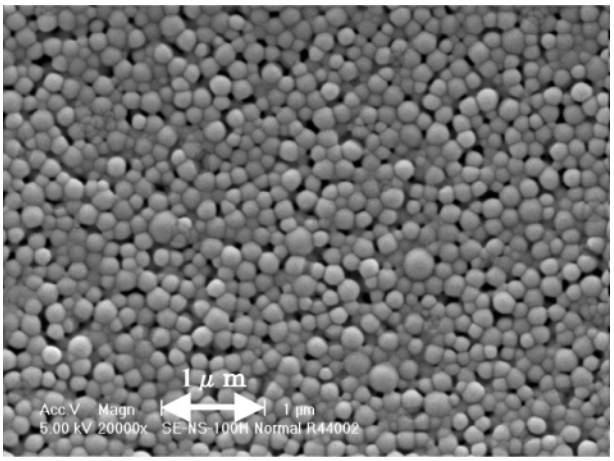

Figure 4. SEM observation of particle size distribution (NS-100H).

achieve non-formaldehyde, different preservatives were added in the dispersion instead of formaldehyde in our all products. Off course these preservatives does not include carcinogen and mutagenicity products.

4.3. Organic Solvent

There is a case that the organic solvents are used in the emulsification process. In the mechanical emulsification method, first, the tackifier resins are dissolved in toluene, and these are emulsified in water with adding the emulsifiers. Following the emulsification, the solvents are removed by distillation under reduced pressure. However, solvents cannot be completely removed and a very small amount remains in the tackifier dispersion. Same as formaldehyde, "Ministry of Land, Infrastructure and Transport" in Japan indicated the guideline value for indoor air concentration of toluene, too. Therefore, complete removal of toluene is required.

In order to solve the problems, two methods were investigated. In the case of the resin having softening point more than 125°C, the mechanical emulsification method was used, but instead of toluene, cycloaliphatic solvents like cyclohexane having lower toxicity compared with toluene was used. By this improvement, new environmentally-friendly tackifier dispersion, toluene-free type "SUPER ESTER NT" series were developed as shown in Table 4.

On the other hand, in the case of the resin having softening point less than 125°C, the phase-inversion emulsification method, in which the solvents were not used in all process, was investigated. In general, because this process provided a large and wide particle size distribution for the dispersion, its stability was not super. In addition to this, a large amount of emulsifier is necessary for stabilizing the dispersion. By optimization of the emulsifier and emulsification condition, the tackifier dispersion having small and narrow particle size distribution could be obtained (shown in Figure 4), and its stability could be improved with minimizing the amount of emulsifier. Thus, the other type of new environmentally-friendly tackifier dispersion, solvent-free type "SUPER ESTER NS" series were developed.

5. Adhesive Performance

5.1. PSA

Test procedure: PSA was prepared by mixing a com-

Table 5. The effect of MS-series tackifier on the adhesive performance

Item \ Products	Untackified	Super Ester				Super Ester	
		NS-100H	NS-125A	NS-100A	NS-120B	E-720	E-650
PE 180° peel [g/in.]	350	580	545	515	540	510	630
Boll tack	11	9	7	8	8	9	7
Shear [h]	>24	8.0	>24	8.5	>24	8.2	>24
Characteristics		Solvent free				Conventional type	

Table 6. The effect of MS-series tackifier on the adhesive performance

Item \ Products	Untackified	Super Ester		Tamanol	Super Ester	
		E-625-NT	E-865-NT	E-200-NT	E-720	E-650
PE 180° peel [g/in.]	350	550	680	600	510	630
Boll tack	11	7	7	7	9	7
Shear [h]	>24	>24	>24	>24	8.2	>24
Characteristics		Toluene free			Conventional type	

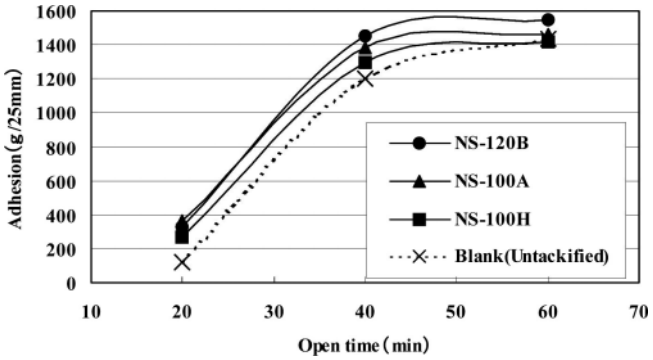

Figure 5. Addition of tackifier in floor adhesive.

mercially available acrylic polymer dispersions with the tackifier dispersions. In this case, the tackifier dispersion was added 10 wt% to the acrylic polymer dispersion by solid base. The testing sample was prepared by direct coating to PET film (38 μm) with a thickness of 30 μm. This sample was dried for 5 min at 105°C and conditioned 24 hr at 23°C/50% relative humidity. Bonds were applied with a 2 kg roller.

Peel: 180° peel (PSTC-1). Adherent is polyethylene. Peel rate 300 mm/min.

Ball tack: J. Dow method.

Share: PSTC-7. Time to failure recorded. 1 inch^2, 60°C, 1 kg, 24 hr.

Summary: The results of the adhesive performance test are shown in Table 5 and Table 6. All of NS-series show the higher peel strength more than E-720, which is conventional and general purpose type. NS-125A and NS-120B show the high shear, about the same as E-650, which is conventional and heat-resistance type. NS-series can achieve the solvent free and the high adhesive performance at the same time.

NT-series show the high adhesive performance, too. Especially, the peel strength of E-865-NT and E-200-NT are excellent. These new environmentally-friendly tackifier dispersions have been used adjusting to the purpose and the environmental level.

5.2. Floor Adhesive

Test procedure: Floor adhesive was prepared by mixing the following materials; acrylic polymer dispersion / tackifier dispersion / $CaCO_3$ / additives (such as a plasticizer) = 100 / 70 / 250 / 40 by solid base. This adhesive was coated on a cement board. After the appointed dry time (open time), a flooring sheet was bonded with the cement board using a 10 kg roller, and immediately, 90° peel strength was measured.

Summary: By addition of NS-series tackifier dispersions in the floor adhesive, the initial peel strength increases up to 40 minutes open time. Especially, NS-100A and NS-120B, which has acid value, indicates higher peel strength.

6. Conclusion

This presentation described the measures of Arakawa Chemical for recent environmental issues of tackifier dispersions, especially “endocrine disruptors” and “indoor air quality”. New environmentally-friendly tackifier dispersions, NT-series and NS-series can achieve both the solutions for each environmental problem and the high adhesive performance at the same time.

Finally, further more improvement of adhesive performance is desired, for example, water resistance, suitability for high speed coating, and so on. By developing the high performance tackifier dispersions and introducing them to the adhesive market, Arakawa Chemical will make continuous contribution to development of the adhesive industry.

References

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