FUNCTIONAL ESTERS DERIVED FROM FATS AND OILS

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ABSTRACT

The fatty acid esters have been used in almost all fields of industry because of their flexibility for desired properties and functions. Actually various kinds of esters with different kinds of performances are designed by changing the starting materials, such as fatty acids and alcohols. That is why fatty acids esters have received considerable attention year after year and they have been used in a lot of fields, such as lubricants, anti-static agents for plastic, cosmetics and so forth.

Recently, the rapid developments of machinery and technology compel fatty acid esters to have much higher performances to meet them. For instance, in the electronic material field, the toners used for electronic photograph required much higher performances in view of energy-saving and high quality picture technology. In order to meet these demands, the wax must fill the properties such as sharp melting point, high heat stability, good colour performance and good dispersibility to resin. Carnauba wax has been one of the most popular waxes and has been used in toner area, but now they are not enough to match these properties needed.

On another front, environmentally friendly lubricating oil is called for more and more in recent years. In the past, mineral oils are conventionally used having the advantage of price. But now good biodegradation as well as excellent heat resistance and good lubricity is fundamental to lubricants used. Especially, the soil and water pollution issue caused by leaking oils from the machine forces to improve and develop new types of fatty acid esters with appropriate combination of properties.

From the viewpoint of environmental friendliness and complex performances desired, fatty acid esters have more possibility to be used in various field of industry due to the reconfiguration of fatty acid moiety and alcohol moiety.

Keywords: fatty acid ester, wax, biodegradable lubricants, high purity solid ester.

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INTRODUCTION

There are many kinds of chemical compounds that are derived from natural oils and fats, such as palm oil and so forth. As examples of fatty acid derivatives, there are alcohols, metal soaps, esters, amides, amines, and many surface-active agents including soaps, and they are now indispensable materials to our daily life. Among these fatty acid derivatives, ester compounds are actually used in almost all fields of industry. The typical applications of fatty acid esters are summarized in *Table 1* (Hirao, 1997).

As *Table 1* shows, fatty acid esters are used most frequently for resin addition agents. The main compound is an aromatic ester, dioctyl phthalate, which is obtained through the reaction of synthetic alcohol and aromatic carboxylic acid. It is mainly used as plasticizer for resin. As far as fatty acids are concerned, one of the most important application fields is lubrication for resin.

Besides the resin addition agents, the applications of fatty acid esters include pharmaceuticals, foods and cosmetics, and various kinds of lubricants. In the former field, fatty acid esters are used as emulsifier, and in the latter, they are used as base oil

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and oiliness improver. In each application, the most appropriate type of fatty acid ester is sorted and used.

TABLE 1. APPLICATIONS OF FATTY ACID ESTERS

Field	Application	Type of esters
Polymers	Plasticizer Slipping agent (lubricant)	Diester Polyol ester Mono ester
Pharmaceuticals, foods and cosmetics	Emulsifier	Sorbitan ester, glycerol monoester, *etc*
	Oil component	Glycerol triester, *etc*
Lubricants	Oiliness improver	Mono ester
	Base oil	Diester Polyol ester

Table 2 shows the typical fatty acid esters and their applications (Hirao, 1997). Most of the fatty acid esters are classified into three types of categories, monoesters, diesters and polyol esters on each structure. Monoesters are synthesized from monohydric alcohols and monobasic carboxylic acids, and are used as metalworking fluids, oiliness improver, *etc*. Diesters are synthesized from monohydric alcohols and dibasic carboxylic acids, and are used for engine oils, compressor oils, *etc*. Polyol esters are the generic designations of neopentyl glycol esters, and are synthesized from neopentyl alcohols and monobasic or polybasic carboxylic acids, and are used for engine oils, refrigerator oil, *etc*. Especially in the polyol esters, *oligo esters* which are synthesized from neopentyl glycol and monobasic carboxylic or dibasic carboxylic acids, are called *complex esters* as trivial name. In addition, the partial esters of polyhydric alcohols, such as glycerin, poly glycerin and sorbitol *etc*., and mono carboxylic acids are used as emulsifiers, *etc*.

It is important to remember that the characteristics of fatty acid esters are different from each other and also can be designed to meet the requests of customers by selecting appropriate combination of alcohols and fatty acids. In other words, fatty acid esters could change their characteristics on the basis of remaining amounts of starting materials of alcohols and fatty acids, alkyl distribution of raw materials and the existence of impurities.

High purity solid esters that are used as wax for toner and the base oil of biodegradable lubricating oils are discussed.

HIGH PURITY SOLID ESTERS

Solid esters have been primarily used as lubricants for resin. But conventional solid esters are commonly prepared using the mixture of fatty acids with wide distribution of alkyl chains. In addition, they usually have a lot of impurities, such as the decomposition materials generated during the production. It will be appreciated that characteristics of solid esters are significantly influenced by the impurity and alkyl distribution of the product. Therefore, the lack of the attention for them sometimes results in the lack of the desired performance.

In order to take concerted action with the rapid advance of the technology in electronic material field, it is necessary to pull out the characteristics of the solid esters sufficiently and apply them for practical use immediately. For the reason above-mentioned, solid ester for electronic materials fields are requested to be very pure as much as possible and to have high design freedom.

TABLE 2. TYPE OF ESTERS AS LUBRICANTS

Type of esters	Structure	Typical product	Application
Monoester	RCOOR'	Butyl stearate	Metal working fluid
Diester	R'OCO-R-COOR'	Di-isodecy ladipate (DIDA) Di-octyl sebacate (DOS)	Automobile engine oil Compressor oil Turbine oil Bearing oil
Polyol ester	(RCOOCH2)X-C-(R')Y	Pentaerythritol tetraheptanoate Trimethylolpropane coco-fatty acid triester	Automobile engine oil Compressor oil Turbine oil Hydraulic fluid Metal working fluid Grease Refrigerating machine oil

High purity solid ester is used as wax for toners because of their excellent characteristics. *Table 3* shows the characteristics of high purity solid esters, WE (waxed ester) series (Sawada, 2003). As it indicates, the low numbers of the acid value and the hydroxy value mean that there are little amount of unreacted materials of fatty acid, alcohol and the decomposition materials in the products. The low number in the hue means that the decomposition of materials is inhibited or removed efficiently.

Especially in the toner use, high quality in the colour is required because of its esthetic preference. Therefore, the request for solid ester varies depending on the variety of toner, manufacturing conditions of toner, variety of resins and additives to use and design concept. Because of these factors, it is necessary for solid esters to be able to meet all manner of requests of melting point for the solid esters.

As it is well-known, the melting points of ester compounds are easy to change by modifying the starting materials, fatty acid and alcohol, and upgrading the refining. It should also be appreciated that solid esters would be stable at higher temperature where toner is usually used.

Thermogravimetry (TG) is sometimes used to characterize thermal stability and decomposition of materials. *Figure 1* shows the mass changes of waxes measured by TG. In the measurement, three typical waxes, WE-5, conventional solid ester wax and carnauba wax, that is conventionally used as natural wax for this purpose having same melting point as WE-5, were estimated at the temperature range of 50ºC to 600ºC. As the data show that there is some difference in the temperature among the three compounds where mass change starts. The conventional wax and carnauba wax started the mass change at around 200ºC and 250ºC, in the mean time, WE-5 was relatively stable even at about 300ºC. It means that WE-5 is more stable than conventional wax and natural wax at higher temperature range where toner might be used.

TABLE 3. GENERAL CHARACTERISTICS OF HIGH PURITY SOLID ESTERS, WE-SERIES

		WE-2	WE-3	WE-4	WE-5	WE-6
Appearance		White powder	White powder	White powder	White powder	White powder
Colour	(Gardner)	1	1	1	1	1
Acid value	(mgKOH g^{-1})	0.1	0.1	0.1	0.1	0.1
Hydroxy value	(mgKOH g^{-1})	< 3	< 3	< 3	< 3	< 3
Melting point	(ºC)	60±1	73±1	71±1	82±1	77±1
Loss on drying	(wt%)	<0.3	<0.3	<0.3	<0.3	<0.3

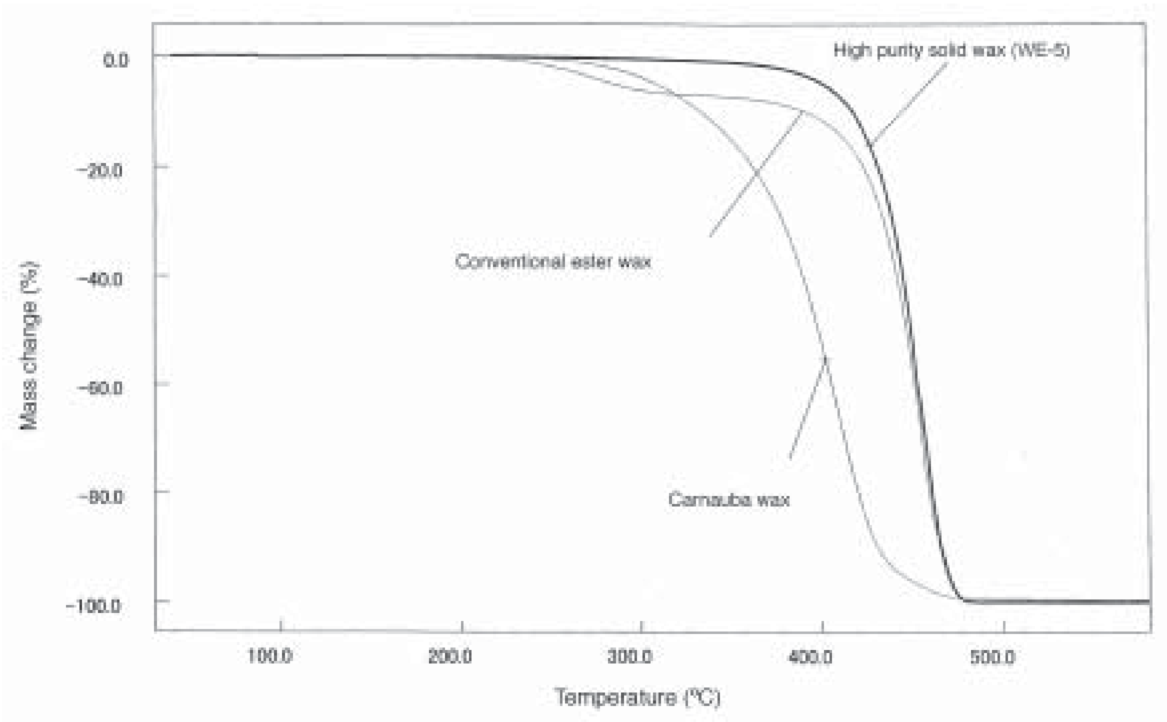

Figure 1. TG curves for WE-5, conventional ester wax and carnauba wax.

Endothermic changes of ester waxes were measured by using differential scanning calorimetry (DSC). In *Figure 2* are shown the DSC melting curves of both high purity ester WE-2 and a conventional one (Sawada, 2003). The data show that the conventional solid ester wax has multiple and broad melting curves at the temperature range of 45ºC to 60ºC. In contrast, WE-3 has only a single narrower melting curve at the higher temperature range than conventional one. It means that WE-3 can stay in a solid state until just before its melting point and melt immediately at the melting point. It is also understood that these heat characteristics make it possible for high purity solid ester WE to possess anti-blocking performance.

Lubricants are usually used under critical conditions such as wide range of temperature and pressure. Because lubricity is considerably influenced by lubricant's viscosity, it is rather preferable to minimize the change of viscosity possibly at the desire range of temperature and pressure.

Figure 3 shows the viscosity data of high purity solid ester (WE) and carnauba wax at the temperature range of 90ºC~150ºC, melting temperature range of carnauba wax. Compared with carnauba wax, WE shows the smaller fluctuation band of viscosity at the measured temperature range and have the lower viscosity near the melting point.

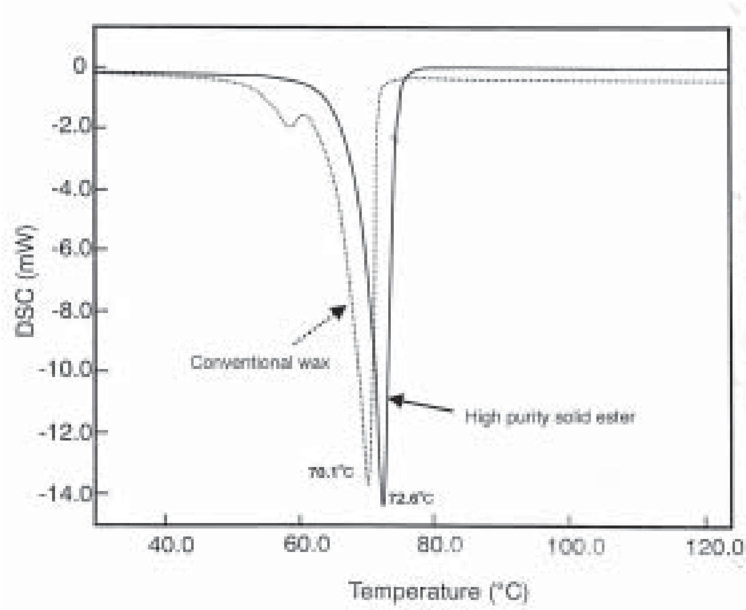

Figure 2. DSC melting curves of WE-3 and conventional ester wax.

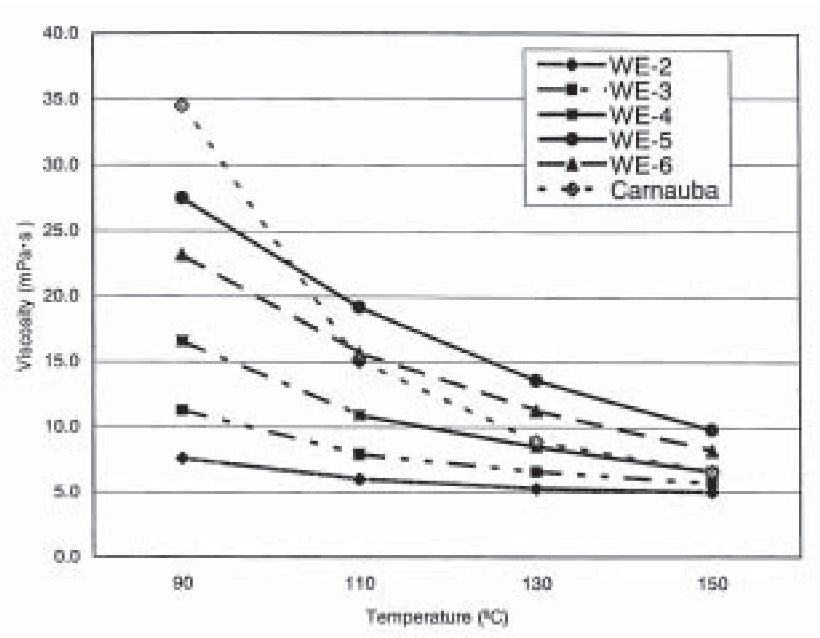

Figure 3. Viscosity of high purity solid.

PRINTING PROCESS OF TONER

The printing process of toner to paper in electronic photographs is illustrated in *Figure 4*. The toner particles stuck on electrostatic drum by static electricity are transcribed on paper, heated and pressed by heating roll, then fixed on the paper. The role of the wax is to melt by heat, seep out of toner resin and help toner resin to fix on the paper and to release it from heating roll. According to the fixing process of toner and the role of wax described above, it is easily understood why thermal behaviours, such as thermal stability, melting point and viscosity, are important key factors when to develop the desired wax for toner. Also, quick response of high purity solid esters to outside heat source makes it possible to reduce the energy that is used in various heating processes in the industry.

Due to the recent enhancement of consciousness for environment, energy saving is one of the most important issues we should deal with, and also we should meet the customer needs and requirements with the advancement of industrial technology. Regarding waxes for toner use, it is absolute to melt quickly at minimum quantity of heat, seep swiftly out of the toner resin and generate desired performance. Furthermore, high heat stability is a must in the heating process of toners. In the preservation and transportation of toner waxes in summer season, rather higher and narrower melting temperature range is desired to prevent melting and accreting under their melting point during the time.

By this means, the high purity solid ester WE with excellent thermal and viscosity characteristics now attract our attentions, especially in the toner wax area of industry.

BIODEGRADABLE LUBRICATING ESTERS

From the enhancement of environmental consciousness in recent years, water pollution and ground pollution caused by lubricating oils are apprehended.

Although mineral oils are the major lubricants used in the various field of industry, they are not biodegradable enough to meet the demands of the times. Actually, as alternatives for mineral oils, there have been developed many kinds of materials, such as polyalkylene glycol, vegetable oils and fats, and fatty acid esters. In Europe, for its own situation, biodegradable hydrauric oils based on rapeseed oils have been developed, placed on the market and used earlier than another region of the world. Polyalkylene glycol has been temporarily used in Europe, but the amount polyalkylene glycol has been decreasing for the sake of the incompatibility with sealing materials or coating materials.

As with Europe, in Japan, environmentally friendly lubricants have received considerable attention, a lot of time and resources have been focused on their development. Japanese Government has enacted an environmental label system *Eco-mark products* officially, where the biodegradable lubricants are registered now.

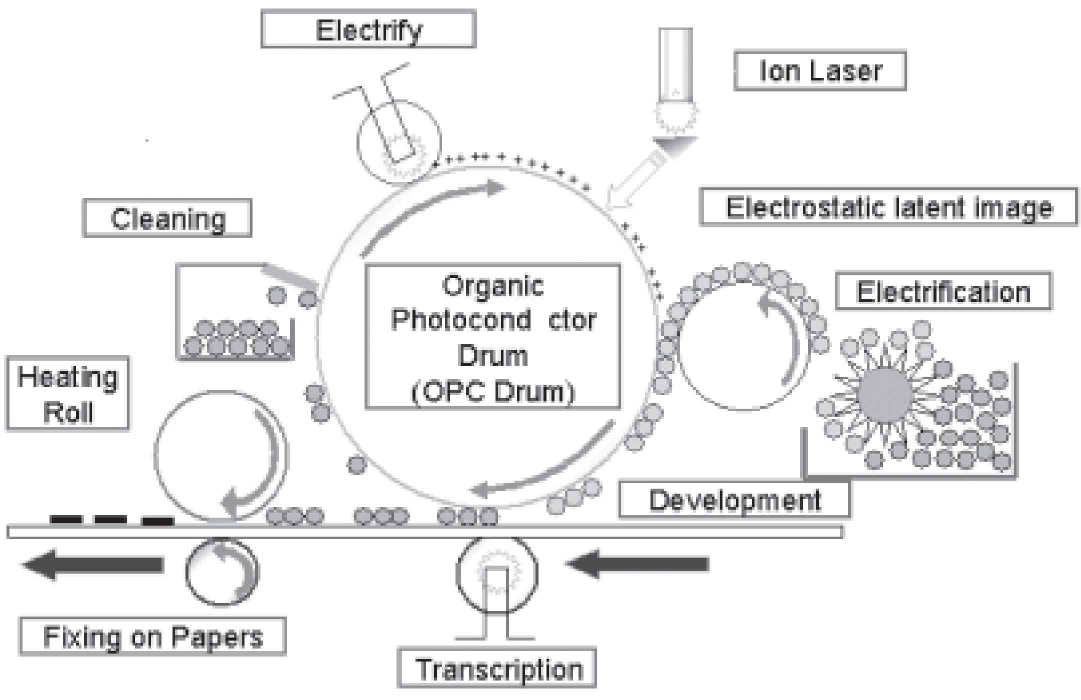

Figure 4. Printing process of toner.

Registration of biodegradable lubricants for eco-mark system is found not only in Japan, but also in Germany *Blue Angel*, Canada *ECOROGO* and northern Europe *Nordic Swan* and so on. Also in International Organization for Standardization (ISO), ISO 15380 for biodegradable hydraulic oils was set up in 2003, where the base oils are classified into four groups (*Table 4*), and the standards for each were defined. For example, for safety test, biodegradable test and toxicity test (acute fish toxicity, acute water flea toxicity and bacteria prevention). On the other hand, for lubricant evaluation, oxidation stability test and wear prevention test have become standard items.

TABLE 4. CLASSIFICATION OF ISO 15380

Name of group	Name in ISO 15380
HETG	Triglycerides (vegetable oil)
HEPG	Polyglycol
HEES	Synthetic esters
HEPR	Poly alpha olefines and related hydrocarbon products

As biodegradable lubricants have been noteworthy for environmental conservation, some fatty acid ester type lubricants are described below.

The data on biodegradability for typical esters are shown in *Table 5*. Although the samples showed desirable biodegradability, for terminal biodegradation, there were some differences between the samples. In concrete terms, the esters with certain characterizing portions, such as branched chain in fatty acid moiety or cross-linking structure by polybasic carboxylic acids, showed the tendency to reduce the biodegradability. As for hydraulic oils, polyol esters or hindered esters of neopentyl polyols have been primarily used.

Since fatty acid esters can be designed in many ways by changing the combination of both fatty acids and alcohols, so it is more important to know the correlations between the structure of esters and characteristics of esters. Then according to the data, it is possible to establish the final structure of ester with desired properties, functions and performances.

The relation between the structure and characteristic of fatty acid esters are shown in *Table 6* (Hirao, 1992). The result of heat stability test of fatty acid esters and rapeseed oil are shown in *Table 7*. Saturated fatty acid ester without double bonds in the structure showed higher heat stability compared with unsaturated fatty acid ester with double bonds in it. High heat stability is one of the most important properties required for lubricating area where lubricants are exposed to high temperature in the friction part. Fatty acid esters can also change the ratio of saturated- and unsaturated-moiety freely, so it is possible to adjust its heat resistance taking other physical properties and performances into consideration.

Typical commercially available lubricating oils, ester type and mineral oil type, are summarized in *Table 8*. As the data indicate, fatty acid esters have rather higher viscosity index compared with mineral oils, and it means that the difference of viscosity between low temperature and high temperature is smaller fatty acid esters. Moreover, the higher flash point of fatty acid esters shows that it can be used as the base oil of fire resistant fluid. *Table 9* shows the result of wear prevention test for lubricity by the vane pump (Shizuka, 1996). It is found that ester-type hydraulic oil has excellent wear resistance compared with that of mineral oil-type hydraulic oil. Therefore, ester-type hydraulic oils can be used under even more severe conditions like higher pressure in hydraulic power unit.

TABLE 5. BIODEGRADABILITY OF FATTY ACID ESTERS

Classification of esters	Type of fatty acids	Biodegradabililty (OECD301C)
Neopentylpolyol ester	Unsaturated, straight, long chain	82
	ditto	80
	ditto	86
	Saturated, straight, middle chain	77
	Saturated, branch, middle chain	68
Complex ester	Saturated, straight, middle chain	68

TABLE 6. CORRELATION BETWEEN STRUCTURE AND CHARACTERISTICS OF FATTY ACID ESTERS

	Lubricity	Viscosity	Viscosity index	Pour point	Thermal and oxidative stability	Hydrolytic stability
1. Increase of chain length	++	++	+	-	-	+
2. Branched chain	--	+	-	+	+	++
3. Unsaturated chain	-	-	±	+	--	±
4. Lack of β-hydrogen in alcohol moiety	±	±	±	±	++	+
5. Increase of -OH groups	+	++	-	±	±	±

Notes: + The increase of corresponding property.
- The decrease of corresponding property.
± No change or sometimes increase and sometime decrease.

TABLE 7. HEAT STABILITY OF FATTY ACID ESTERS AND RAPESEED OIL

			Polyol ester (saturated, middle chain)	Polyol ester (unsaturated, long chain)
Before test	Acid value	(mgKOH g^{-1})	0.1	0.3
	Viscocity at 40ºC	(mm^2 s^{-1})	19.6	48.5
	Viscocity at 100ºC	(mm^2 s^{-1})	4.40	9.76
After test	Colour	(Gardner)	1	1
	Acid value	(mgKOH g^{-1})	0.4	2.2
	Viscocity at 40ºC	(mm^2 s^{-1})	20.8	79.9
	Colour	(Gardner)	7	12
	Volatilization loss	(wt%)	0.88	1.08

TABLE 8. CHARACTERISTICS OF LUBRICATING OILS

	Fatty acid ester (type A)	Fatty acid ester (type B)	Mineral oil (type A)
Acid value (mgKOH g^{-1})	0.53	0.68	0.09
Viscosity at 40ºC (mm^2 s^{-1})	34.12	47.15	30.88
Viscosity at 100ºC (mm^2 s^{-1})	7.307	9.251	5.95
VI (Viscosity index)	188	183	141
Colour (ASTM)	2	2	0.5
Pour point (ºC)	-28.0	-32.0	-41.0
Flash point (ºC)	288.0	286.0	216.0

TABLE 9. WEAR PREVENTION TEST BY VANE PUMP

		Fatty acid ester (Type C)	Fatty acid ester (Type D)	Mineral oil (Type B)
the amount of abrasion* (mg)	50 hr		6.3	
	100 hr	6.7	7.7	20.9
	250 hr		9.0	
	500 hr		11.5	

*Total amount of loss of vane and cam ring in the test.

CONCLUSION

High purity solid esters have been used as the wax for toner, because they have higher heat stability, narrower melting curve and lower temperature dependence of viscosity compared with natural wax and conventional solid esters. Due to their unlimited possibility of molecule design, the esters have received more attention in the new fields of industry, like electronic material field, high function resin field and lubrication field as well.

Moreover, since fatty acid esters have higher heat stability and preferable biodegradability, they have been partially replacing the mineral oils that used to be the mainstream in the lubricating oil fields. Amid an energy crisis and an environmental crisis, environmentally friendly and highly sophisticated fatty acid esters have come under review catering for the requests from customer and society.

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