

# Offset Printing Inks Based on Rapeseed and Sunflower Oil. Part I: Synthesis and Characterization of Rapeseed Oil- and Sunflower Oil-Modified Alkyd Resins

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**ABSTRACT:** Two sets of alkyd resins of variable oil lengths with the required properties for offset printing ink formulations, modified by sunflower and rapeseed oil, were synthesized according to the "monoglyceride" process. The influence of the acyl composition of the modifying vegetable oil and of the oil content on alkyds' properties was determined by detailed chemical and rheological characterization. Molecular structure, size, and molecule size distribution appeared to be linked to these two factors. A comparative study with two usual linseed oil-modified alkyds led to determination of the more appropriate alkyds for applications in offset varnishes.

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**KEY WORDS:** Alkyd resin, fatty acids, offset ink, oil length, rapeseed oil, sunflower oil.

Offset printing inks are multicomponent systems that include "hard resin," alkyd resin, hydrocarbon solvent, pigment, and optional additives. Alkyd resins are polyesters modified with fatty acids. The most commonly used alkyd resins in the printing industry are drying or semidrying oil-modified alkyd resins, mostly linseed oil-based resins, for improvement of the drying characteristics of printed films (1,2). However, the high amount of polyunsaturated fatty acids in drying oils causes an oxidative degradation that involves color instability (3–5). The aim of this work was to formulate efficient offset inks with sunflower oil (SOA)- (semi-drying oil), or rapeseed oil (ROA)- (a nondrying oil) modified alkyd resins, to define the influence of the acyl composition of oil on the alkyds' properties.

The first part of this study is related to the preparation and characterization of sunflower- and rapeseed oil-modified alkyds of variable oil lengths. Oil length refers to the oil percentage of an alkyd. A long oil alkyd contains 60% and more of oil. When oil amounts fall between 60 and 40%, it is a medium oil alkyd. Below 40% oil, the resin is a short oil alkyd. One medium oil length and two long oil length alkyds, which meet as closely as possible the specific requirements of offset printing inks, were prepared respectively with SOA

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and ROA. In a first step, specific properties of the alkyds were established according to the acyl composition of the modifying vegetable oil or to the oil percentage. In a second step, a comparative study of the synthesized alkyds with two common linseed oil-modified alkyds used in heatset and quickset formulations was carried out. Finally, the most appropriate alkyds for application in offset varnishes were determined.

## EXPERIMENTAL PROCEDURES

**Materials.** SOA and ROA were edible-grade. Phthalic anhydride (97%), anhydrous glycerol (98%), and potassium hydroxide (85%) were purchased from Fluka (Buchs, Switzerland). Technical xylene (isomers mixture) was provided by Prolabo (Fontenay-sous-Bois, France). Linseed oil-based alkyds were supplied by Coates-Lorilleux (Thourotte, France).

**Alkyd resins synthesis.** Alkyd resins are basically oil-modified polyesters, formed by condensation-polymerization of polyhydric alcohol, dibasic acid, and fatty acids or oils (6). In our work, alkyds were obtained by the condensation of phthalic anhydride with monoglycerides, which were obtained by transesterification of triglycerides with glycerol. This involved two steps.

**Step 1: alcoholysis.** A mixture of the calculated amount of glycerol (2 moles), oil (1 mole) and potassium hydroxide (0.003%) was placed in a four-necked reaction flask, equipped with an agitator and a Dean-Stark trap. The mixture was heated to 180°C at 20°C/min, under nitrogen atmosphere. Then, agitation was started, and the temperature was raised at 1°C/min. When a temperature of 210°C was reached, the reaction mixture was allowed to cool to ambient temperature, and a solubility test was carried out in methanol: one part of the reaction mixture had to be soluble in three parts of methanol. The product obtained, called "monoglyceride," was in fact a mixture of monoglycerides, diglycerides, triglycerides, and glycerol; the real amount of monoglycerides was approximately 50%.

**Step 2: resins synthesis according to the solvent process.** After formation of the "monoglyceride" (step 1), the calculated amounts of phthalic anhydride and oil were added. KOH

used for "monoglyceride" synthesis was still present and could catalyze the alkyd formation. The reaction was carried out at 205°C, under a nitrogen atmosphere. Xylene was used for azeotroping. When the desired acid number was reached, the reaction was stopped, and the reaction mixture was allowed to cool to ambient temperature.

In this study, three alkyd resins with variable oil lengths were prepared respectively with SOA and ROA: one medium oil length and two long oil lengths.

*Alkyd resin characterization.* Acid and hydroxyl values were determined according to AFNOR methods (NFT 60-221, NFT 60-213) (3).

A controlled-stress Carri-Med rheometer (CSL 100 Model; Carri-Med, Palaiseau, France) was used in the flow mode with cone-plate geometry to determine viscosity (cone diameter, 2 cm; top angle, 4°; stabilization time, 30 min). Measurements were conducted for 3 min at 20°C. Each experiment was repeated four times. The viscosities were determined according to the Bingham mathematical model (7).

Apparent molecular weights of the alkyd resins were obtained by gel permeation chromatography. The chromatographic system consisted of an isocratic pump P 1000 (Model P 1 000; Spectra Physics, San Jose, CA), a refractometer detector Shodex RI-71 (Showda Denko, Tokyo, Japan), and an oven for columns thermostated at 40°C by a CrocoCil temperature regulator (Chromatosud, Bordeaux, France). The chromatograms were recorded, and the peaks were integrated by an SP 4270 integrator (Spectra Physics, San Jose, CA). Three HPSEC Phenogel analytical columns were used (Phenomenex, Torrance, CA). The samples were dissolved in tetrahydrofuran (0.4% wt/vol) and then injected with a six-port Rheodyne 7125 syringe-loading injector valve (Rheodyne, Los Angeles, CA). Chromatography operating conditions were: flow, 0.5 mL/min; columns, 30 cm, 7.5 mm, columns porosity, 100 Å, 500 Å, 1 000 Å; injection volume, 20 µL. Polystyrene standards from Interchim Laboratories (Montluçon, France) had the following peak average molecular weights (MW) and MW distribution (MWD): 760, 1.30; 7000, 1.04; 13000, 1.04; 35000, 1.06. The number and weight average MW (Mn and MW) were easily calculated by entering the relevant masses and peaks into commercial spreadsheet software (GPC Spectra Physics GPC/PC Software).

The electrospray mass spectrometry (MS) spectra (positive ion mode) were recorded with a Fisons VG - Quatro quadrupole-hexapole quadrupole mass spectrometer, equipped with an electrospray ionization source, capable of analyzing ions up to  $m/z$  4000. The temperature of the electrospray (ES) ionization source was maintained at 70°C. The operating voltage of the ES capillary was 3.50 kV, and the high voltage lens was maintained at 0.50 kV throughout.

The solutions used for liquid chromatography (LC)/MS spectra were prepared with high-performance liquid chromatography (HPLC) solvent-grade chloroform/methanol (50:50, vol/vol). A 20-mL aliquot of sample was then introduced into the electrospray ion source at a flow rate of 20 mL/min with a

Shimadzu LC-10AD pump (Tokyo, Japan) connected to the Rheodyne injector.

The tack values were measured with a Tack-o-scope tackmeter (Rudolph Meyer, Amsterdam, The Netherlands) at 30°C. The operating conditions were: alkyd volume (measured with an IGT pipette; IGT, Paris, France), 0.6 cm<sup>3</sup>; testing speed, 100 m/min; distribution time, 1 min.

Methanol and peptizing values were respectively measured by TEC 003/74M and TEC 003/24M procedures (Coates-Lorilleux; TOTAL).

## RESULTS AND DISCUSSION

The composition, oil length, and acid values of the synthesized alkyds are summarized in Table 1. Alkyd samples had a similar acidity, in the range of 7–10, to establish correlations with other parameters linked to the polymerization degree, such as viscosity, hydroxyl value, or MW.

*Average MW.* The Mn and MW, listed in Table 2, were similar for all synthesized alkyds. Polydispersity indices (MWD), around 2, indicate that the size distributions were heterogeneous.

*Mass spectra studies.* The fatty acid composition effect of each oil type on polymer molecular structure was investigated by a comparative analysis of S3 and R3 alkyd spectra (Fig. 1). R3 and R1 alkyd spectra (Fig. 2) showed the influence of the oil rate. Maximum entropy spectra confirmed the alkyds' polydispersity and showed disparities in MWD according to the alkyds' chemical composition. For a given oil length, ROA R3 contained more low-molecular weight species (1000–3000 Da) than SOA S3 (Fig. 1). For a given oil type, the relative abundance of high-molecular weight species (>4 000 Da) increases when the oil length decreases (Fig. 2).

The main ions from fragmentation of the monomer pattern, showed in Figure 3, were detected in all spectra. In the ion-ES mass spectra of R3 and R1 (Fig. 4), practically the same fragments were identified. Ions with a loss of two, four, or six protons corresponded to fragments that contained polyunsaturated fatty acids. For example, the ion at  $m/z$  881 (R: oleic acid) went with ions at  $m/z$  879 (R: linoleic acid) and  $m/z$  877 (R: linolenic acid). The relative abundance of these ions was not proportional to the fatty acid composition of the modifying oil, although fragments with oleic acid were the most abundant. Ions containing linolenic acid were obtained in a relative high abundance despite a low amount of triunsatu-

**TABLE 1**  
Oil Lengths and Acid Values of the Alkyds (SOA and ROA)

Alkyd	Sunflower oil (SOA)			Rapeseed oil (ROA)		
	S1	S2	S3	R1	R2	R3
Oil length (%)	58.5	65.5	68	58.5	65.5	68
Acid value (mg KOH/g)	9.5	7.8	8.1	9.3	9	8.3

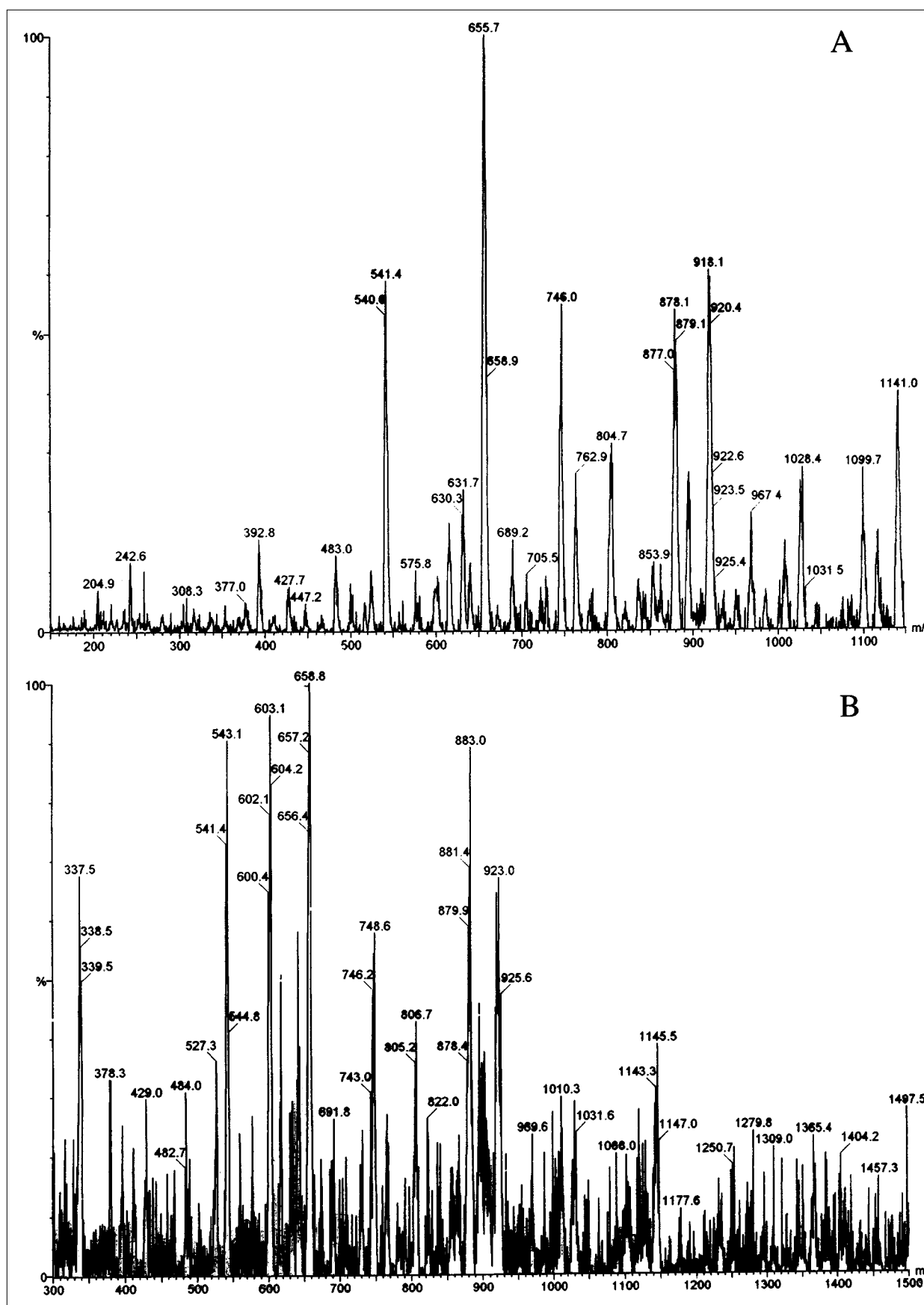


FIG. 1. Mass spectra of the alkyls (A) S3 and (B) R3.

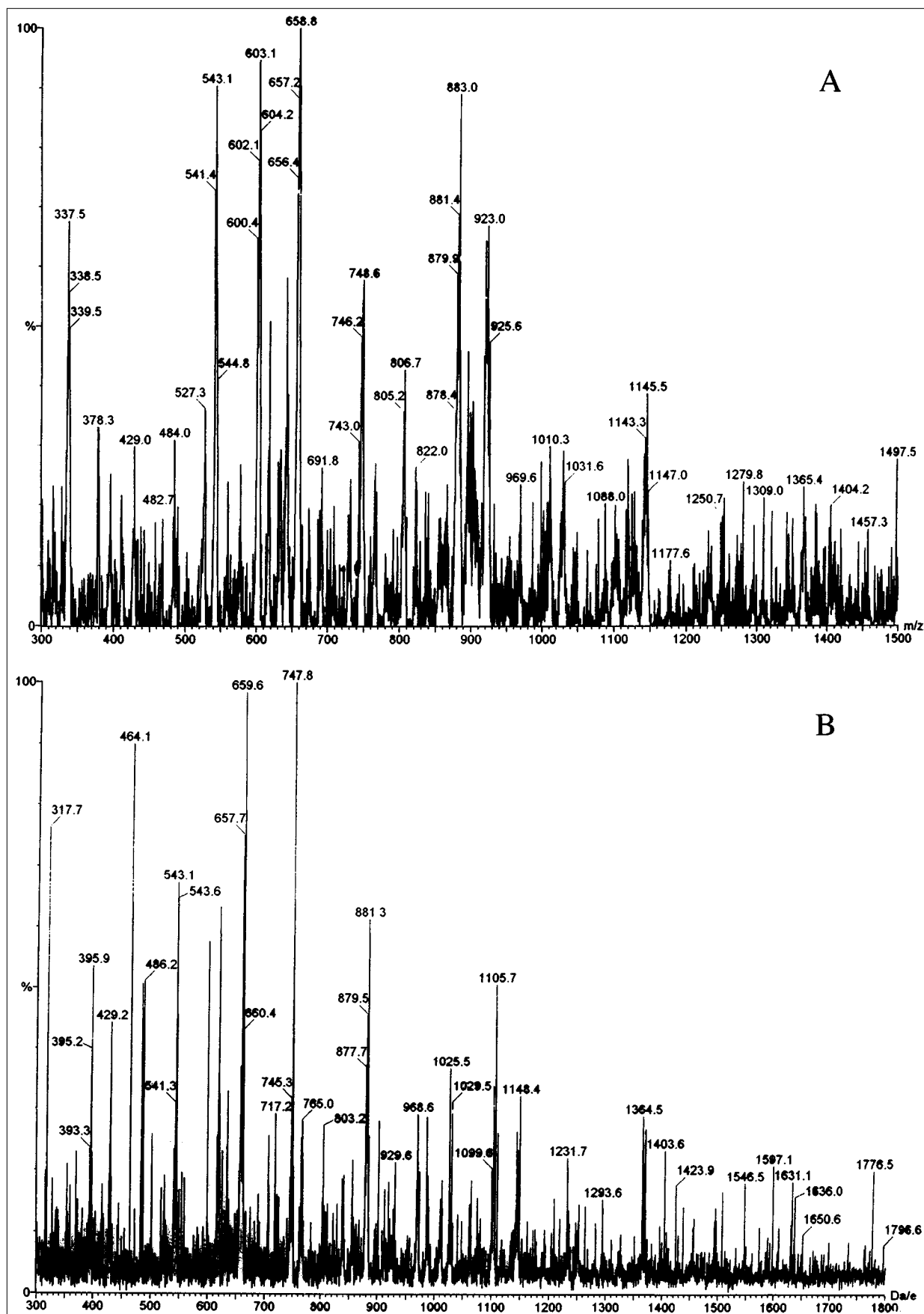


FIG. 2. Mass spectra of the alkyls (A) R3 and (B) R1.

**TABLE 2**  
**Alkyd Molecular Weights**

Alkyd	Sunflower oil (SOA)			Rapeseed oil (ROA)			Linseed oil standards	
	S1	S2	S3	R1	R2	R3	L1 (heatset)	L2 (sheetfed)
Oil length (%)	58.5	65.5	68	58.5	65.5	68	84	72
$M_p$	3700	3600	3700	3600	3700	3500	8900	14200
$M_n$	1900	1900	1850	1900	1900	1750	2600	2700
MWD	1.95	1.95	2	1.9	1.95	2	3.4	5.3

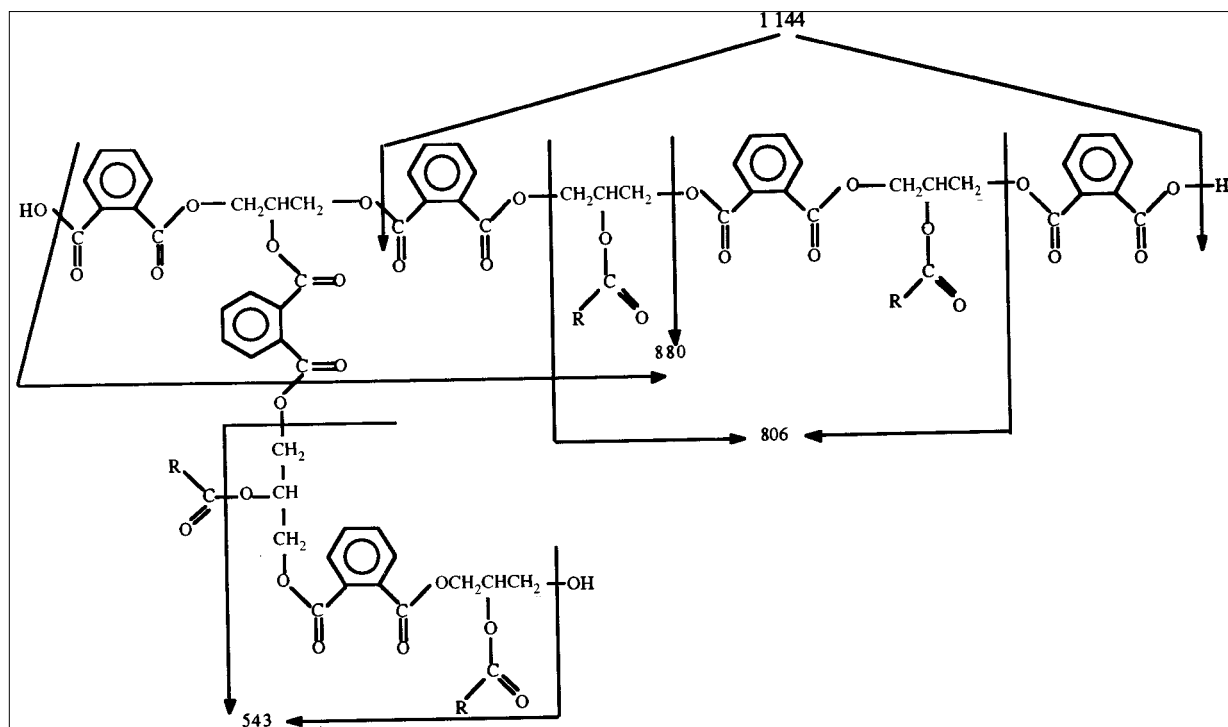
rated acids in the initial oil. So, monoglycerides of triunsaturated fatty chains could be more reactive during polycondensation than the others.

For a given oil length, the SOA-modified alkyd spectrum S3 showed a lower abundance of low-weight ions than the ROA-based alkyd R3 spectrum (Fig. 5). Probably, SOA was more reactive during the alkyd synthesis than ROA. Identified ions at  $m/z > 500$  in the ROA spectrum R3 are present on the SOA spectrum S3. However, they came from fragments containing linoleic acid, the major fatty acid in SOA: during SOA synthesis, linoleic acid was the most reactive fatty acid; during ROA synthesis, the polyunsaturated fatty acids were in opposition, and no predominance was observed.

The fatty acid composition of the modifying vegetable oil and oil rate control the molecular structure and the particule size distribution of the alkyd resin.

*Viscosities.* Viscosities, expressed in Pa.S, are listed in Table 3. The viscosity parameter is linked to the particule size and to the cohesive energy of the polymers. First, for a given oil type, a drop of the oil content results in a greater abundance of higher-molecular weight species (cf. mass spectra studies). Secondly, because of the drop of the fatty chain amount, free hydroxyl sites are more numerous, and steric blocking is lower. Therefore, there are greater amounts of intra- and intermolecular hydrogen bonding and the cohesivity of the polymers is stronger, and thus the viscosity is higher.

For a given oil length, the ROA samples were more viscous than the SOA samples. Alkyd viscosity was linked to the acyl composition of the modifying oil. ROA, more viscous than SOA, led to more viscous alkyds (8). This result could also be attributed to the presence of a more reactive fatty acid, linolenic acid, in rapeseed oil. At the temperature of alkyd


**FIG. 3.** Main fragmentations of the monomer pattern.

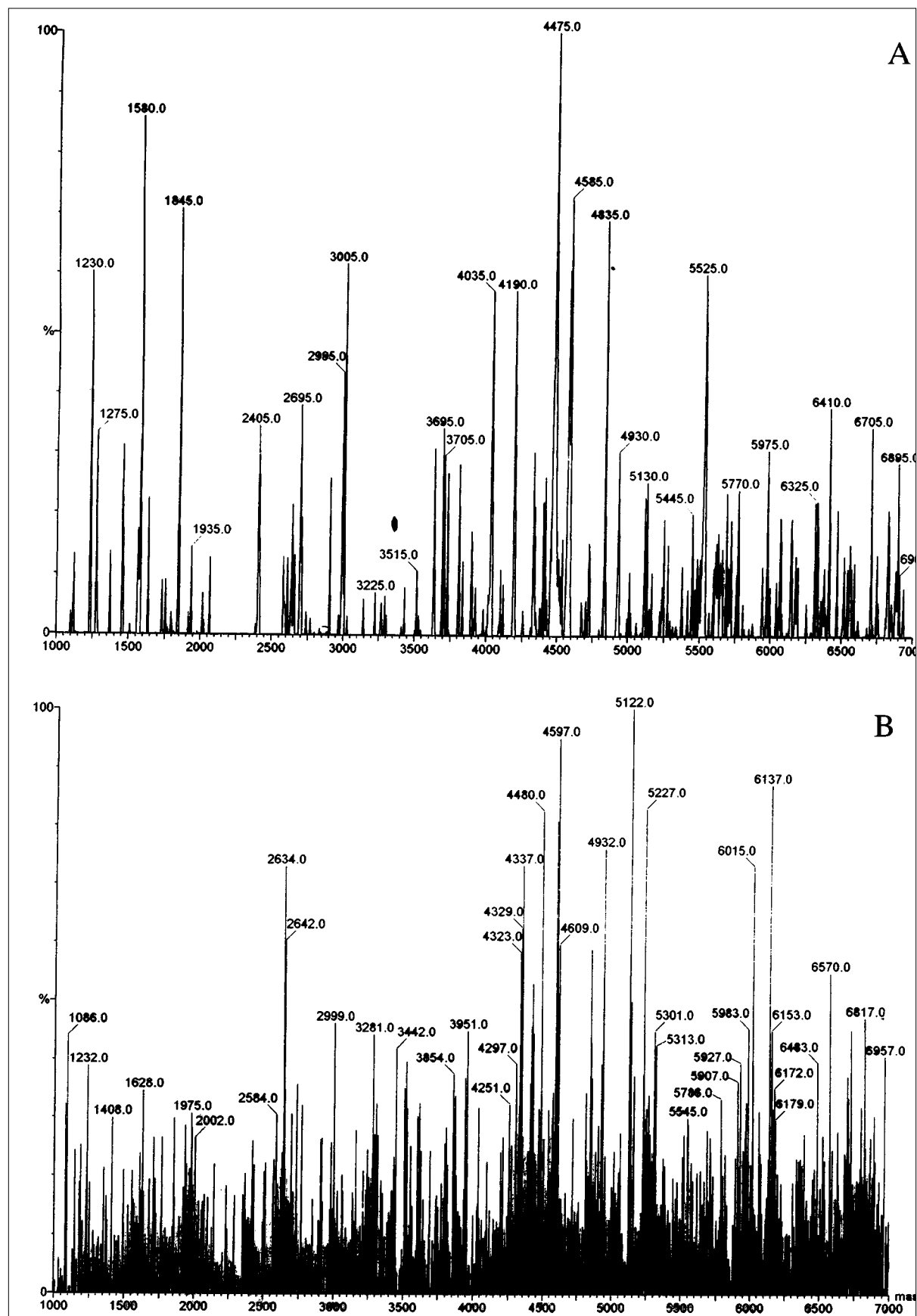


FIG. 4. Maximum entropy mass spectra of the alkyds (A) R3 and (B) R1.

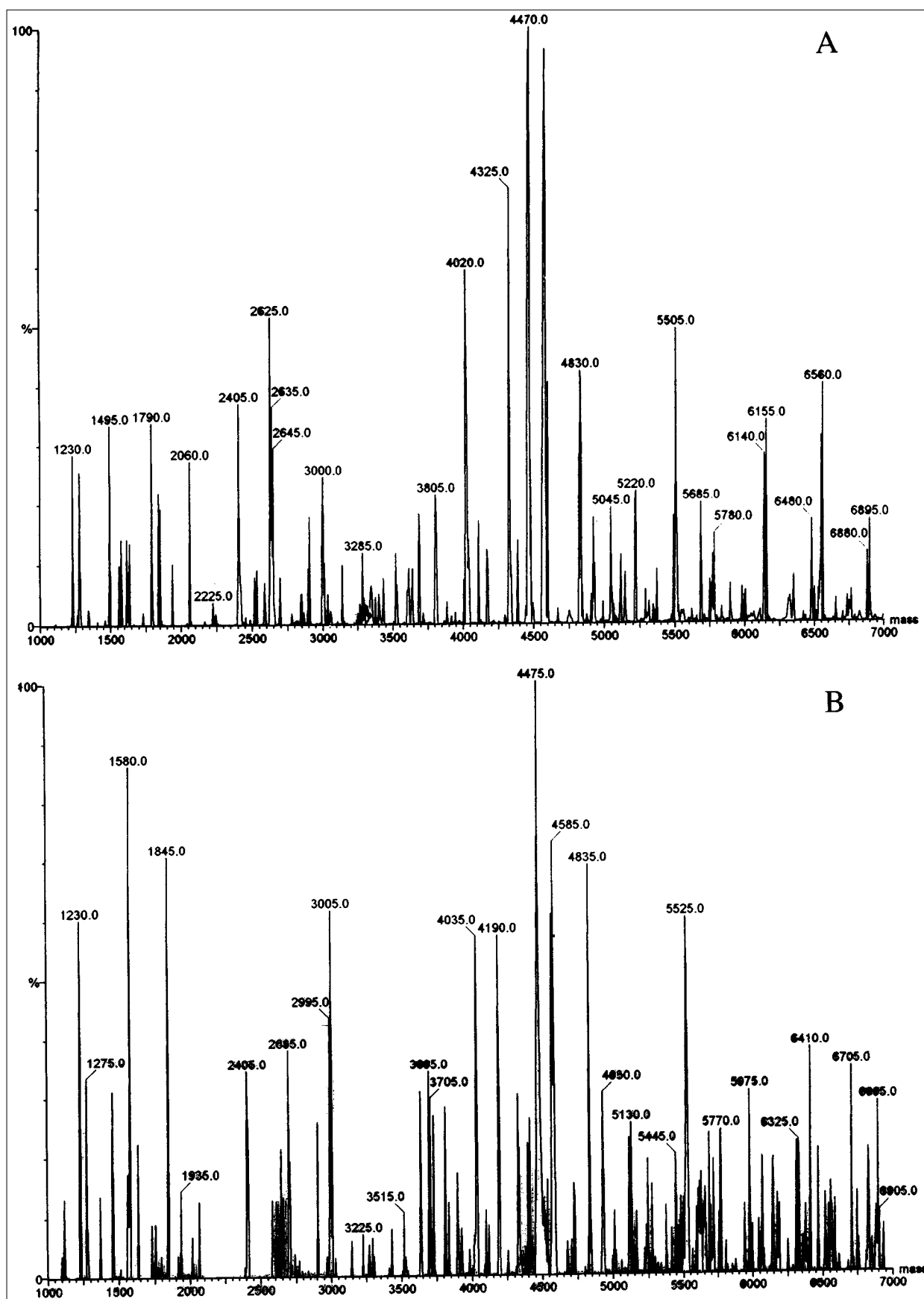


FIG. 5. Maximum entropy mass spectra of the alkyds (A) S3 and (B) R3.

**TABLE 3**  
**Alkyds Characteristics**

Alkyd	Sunflower oil (SOA)			Rapeseed oil (ROA)			Linseed oil standards	
	S1	S2	S3	R1	R2	R3	L1 (heatset)	L2 (sheetfed)
Oil length (%)	58.5	65.5	68	58.5	65.5	68	84	72
Viscosity (20°C, Pa.S)	45.1	7.8	4.4	55	11.9	4.6	20–35	5–12
Hydroxyl value (mg KOH/g)	55	36	28	51	33	26	<40	<35
Methanol value (cm <sup>3</sup> )	60	52	52	64	53	53	30–35	27–31
Peptizing value (°C)	32	38	35	40	43	40	37–43	35–41

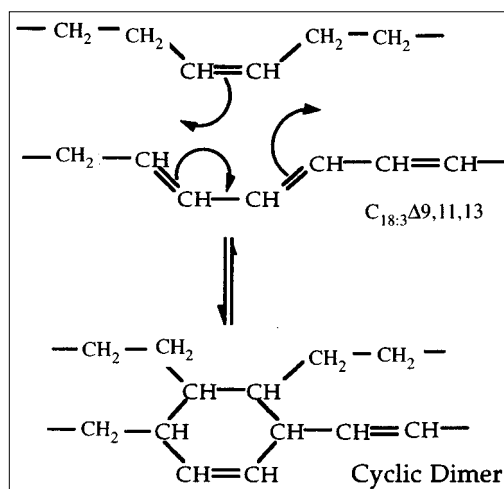
synthesis, the polyunsaturated bonds of the fatty acids could migrate, and conjugated polyenes could be formed (8). Then, the conjugated fatty acids could react with other unsaturated fatty acids to form dimers according to Scheme 1. Isomerization reactions were less important for SOA because of its fatty acid composition (linolenic acid is more reactive than linoleic acid). Probably, these specific dimerization reactions could explain the lower abundance of high-weight fragments, above 3 000 Da, of the ROA by steric blocking, which limited polymerization.

**Tack measurements.** In the printing industry, the tack of an alkyd, a varnish or an ink, reproducing the transfer of these products through the presses or the transfer to paper, is an important quality. Tack can be described as the force per unit area required to split a film between two surfaces (9). The tack values were measured to evaluate alkyd stability by using a system that reproduces press conditions. Tack kinetics are represented in Figure 6. For each oil type, the tack values increase when oil length decreases. So, the shorter oil alkyds R1 and S1 were characterized by high tack values and

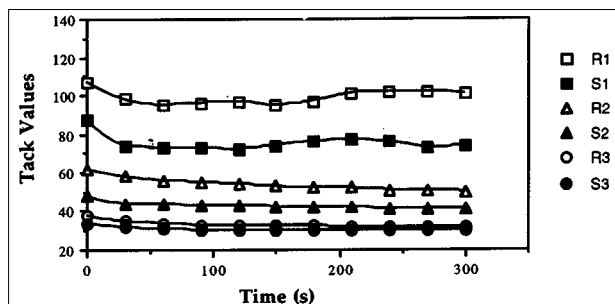
a slightly instable behavior because of the high viscosities and cohesivities of these products. R2, S2, R3, and S3 alkyds seemed to be more adapted to ink formulation. For a given oil length, SOA showed lower tack values than ROA. Specific space arrangements of the fatty chains according to their nature, and numerous dimerization reactions, could explain the higher tack values of the ROA.

**Solubility characteristics (Table 3).** Methanol value permitted an evaluation of alkyd compatibility with traditional solvents used in ink varnishes. Methanol value increased when the possibility to form secondary bonds with the alkyd increased. So, the solvent tolerance was linked to oil length, and the shorter oil length alkyds, R1 and S1, were characterized by the higher methanol values. Resin solvation was easier when the hydroxyl sites were more numerous and when the steric blocking caused by fatty chains was lower. The solvent tolerance was not linked to the nature of the modifying oil.

Alkyd solubility in a specified varnish is related either to the alkyd affinity with the hard resin or to solvation by petroleum distillates. The highest soluble alkyds present the strongest affinities for a specified system of hard resin-solvent(s). First, alkyd resins, diluted in saturated hydrocarbon apolar aprotic solvents, tend to be associated (10). This tendency and the stability of the formed complexes become higher either with the number of hydroxyl functions or the chain's symmetry because formation of hydrogen bonds is



**SCHEME 1**



**FIG. 6.** Tack values of the rapeseed oil and the sunflower oil.



easier (11). Second, alkyds diluted in poor solvents adopt a conformation that favors intra- and intermolecular interactions (12). For each oil type, the intermediate oil alkyd is the most peptizing. The weak affinity of the "hard resin" with the shorter oil alkyds, insufficient to dissociate the linked alkyd molecules, explained the lower solubility of the R1 and S1 samples. The decrease of solubility of the longer alkyds, R3 and S3, could be attributed to a lack of interactions with the "hard resin," caused by the decrease in hydroxyl content.

In all tests, greater peptizing values of ROA than SOA were noticed. Specific molecular structures and specific particule size distributions, according to the nature of the modifying oil used, could explain these differences. Dimers that occur in ROA resulted in more appropriate molecular edifices, in lower particule size, and probably in more adapted chain conformations, and favored solubilization of the alkyds in these varnishes.

*Comparative study.* The application ranges of the synthesized alkyds were determined by carrying out a comparison with two alkyd types used in offset formulations. These two reference alkyds, noted L1 and L2, constituted of pentaerythritol and isophthalic acid, were modified by linseed oil, a good drying oil. The synthesized alkyds and reference characteristics are summarized in Tables 2 and 3.

*Comparison with alkyd L1 in heatset varnishes.* ROA- and SOA-based alkyds, whatever the oil content, presented smaller average MW and lower polydispersity indices (MWD) than alkyd L1 (Table 2). However, alkyds R2 and S2 showed similar viscosities with the reference L1 (Table 3). This could be explained by the specific chemical composition of the two reference alkyds, resulting in specific molecular structures, and thus in different properties. ROA and SOA showed stronger solvency tolerances than alkyd L1, whatever the considered oil rate. Lower size particules and probably more adapted conformation chains of glycerophthalic alkyds facilitated the interactions with hydrocarbon solvents. The four longest oil alkyds, R2, S2, R3 and S3, had appropriate peptizing values although the highest solubilities of the ROA seemed to be more adapted to the formulation of heatset varnishes.

*Comparison with alkyd L2 in quickset varnishes.* In the same way, ROA and SOA presented lower average MW and a lower particule size distribution (MWD) than linseed oil-based alkyd L2, but the differences were more important than in the previous comparison. The most appropriate viscosities corresponded to an intermediate oil percentage situated between 58.5 and 65.5% (Table 3). However, alkyds R2 and S2 were characterized by the most suitable hydroxyl values. Solubility characteristics of alkyd L2 were similar to those of alkyd L1 (Table 3).

The first step of this study consisted of the characterization and evaluation of two sets of alkyds, based respectively

on ROA and SOA, for offset varnish and ink formulation. Specific properties were noticed according to vegetable oil nature and to oil content. The chemical structure and the MWD of these alkyds were linked to these two parameters: ROA results in alkyds characterized either by a lower abundance of high-molecular weight species or by specific molecular structures (dimers involving linolenic acid), resulting in stronger viscosities, higher tack values, and greater peptizing values than SOA.

In spite of different size distributions from the two references L1 and L2, ROA and SOA met largely the specific requirements of offset printing inks. Replacing the usual alkyds by these new alkyds in offset varnishes, without modifying the established formulation, is now necessary to confirm the first results obtained. The formulation and characterization of offset varnishes based on ROA and SOA will be described in a following article (Sabin, P., B. Benjelloun-Mlayah, and M. Delmas, submitted for publication).

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