Offset Printing Inks Based on Rapeseed Oil and Sunflower Oil. Part II: Varnish and Ink Formulation

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ABSTRACT: Two sets of variable oil length, alkyd resins modified by sunflower oil (SOA) and by rapeseed oil (ROA), were evaluated in offset formulations with mineral oils as diluent. The more suitable alkyds for this kind of application were determined. In a second experiment, hydrocarbon solvents were substituted by the fatty acid methyl esters derived from rapeseed oil or sunflower oil to produce ecologically friendly offset printing inks. Finally, the ROA and the SOA were associated with the methyl esters derived from the same vegetable oil. New properties of the varnishes composed of a vegetable diluent were evaluated. The quickset formulations with the methyl esters do not need important modifications, as opposed to the heatset formulations.

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KEY WORDS: Drying properties, heatset formulation, methyl ester, offset printing ink, quickset formulation, rapeseed oil-modified alkyd, sunflower oil-modified alkyd, varnish.

Offset printing inks, usually composed of "hard" resin, alkyd resin, hydrocarbon solvent, pigment and additives, are petroleum-based mixtures. Since the beginning of the 1980s, the American Newspaper Publishers Association (ANPA) has investigated the possibility of formulating nonpetroleum inks by replacing hydrocarbon solvents with vegetable oil. For the first time, many newspaper printing inks were formulated with tall oil as diluent (1–3). Later, ANPA workers proposed more successful formulations with soybean oil (4–6). In sheet-fed and heatset printing inks, the attempts were inconclusive, especially for heatset printing. In 1991, Erhan and Bagby (7–10) obtained vegetable oil-based vehicles by thermal transformation of some vegetable oil starting materials with various degrees of success.

The purpose of this work was to formulate new ecologically friendly offset printing inks that answer both to ink makers' and agricultural problems, and to search for successful printing inks that contain a large portion of vegetable oil and do not require any petroleum components. Rapeseed oil (ROA) and sunflower oil (SOA) were preferred to those vegetable oils that are usually used in offset ink formulations, such as linseed oil or soybean oil, for economic and availability reasons.

Part I of this series (11) reported on the synthesis and characterization of two sets of variable-oil-length alkyds, modified by ROA and sunflower oil (SOA), that possessed the required properties for offset printing ink applications. Chemical characteristics and properties of these oleoglycerophtalic alkyds appeared to be linked both to the modifying vegetable oils fatty acid composition oil and oil content. Finally, all synthesized alkyds seemed to be adapted to offset varnish formulations, although the two shorter alkyds, R1 and S1, showed less appropriate behavior.

Part II of this study reports on the practical evaluation of these alkyds in offset varnishes to determine resins that suit this type of application. The ROA and SOA were evaluated in varnishes for heatset printing before being tested in varnishes that contain more alkyd resin for sheet-fed printing.

The second objective was to substitute the toxic and polluting hydrocarbon distillates with vegetable diluents to produce "green" offset inks. However, triglycerides, being heavy and viscous compounds, cannot be used as such in this type of formulation especially in heatset formulations that require a very volatile liquid fraction. However, the methyl esters derived from ROA or SOA seem to have more adaptable characteristics. A second step replaced the mineral oil portion with methyl esters in formulations based on a linseed oil-modified alkyd resin. These substitutions were first attempted in quickset formulations that do not require a volatile fraction. Finally, the ROA or SOA was associated with the vegetable oil derivatives to yield petroleum-free printing ink formulations. The varnishes were all pigmented in accordance with the required specifications, and the inks were printed to confirm the predicted results.

The ROA and SOA are based on less drying vegetable oils than the usual alkyds that have been modified by drying oils; this could result in a decrease of oxidative drying achievement of the printed films. The fatty esters, characterized by the presence of the reactive ester function and by specific fatty chain conformations according to their degree of unsaturation, should behave differently in offset formulations than the inert mineral oils. Therefore, the alterations of the varnish and ink properties caused by these new products, in particular modifications in drying properties, have been determined and discussed.

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TABLE 1
Characteristics of the Hard Resins A and B

	Resin A	Resin B
Viscosity (40% resin/60% xylene) (Poises-Laray/23°C)	12	120
Softening point (°C)	150	170
Methanol value (cm^3)	63	15
Peptizing value (cm^3)	32	25
Solubility	Strong	Low

TABLE 2
Formulations of the Heatset Varnishes with Mineral Oils as Diluent (per 100 g)

Varnish	Standard A1-L1	A1-R3	A1-S3
Resin A (g)	39	39	39
Alkyd L1 (g)	14	—	—
Alkyd R3 (g)	—	14	—
Alkyd S3 (g)	—	—	14
Mineral oil 240–270°C (g)	23	23	23
Mineral oil 260–290°C (g)	24	24	24

EXPERIMENTAL PROCEDURES

Materials. The ROA-modified alkyds R1, R2, R3, and R4, and SOA-modified alkyds S1, S2, S3, and S4, were synthesized according to an experimental procedure described in part I of this series (11). The linseed oil-based alkyds (L1, L2) and hydrocarbon solvents were supplied by Coates-Lorilleux (Thourotte, France). The "hard" resins A and B, provided by Coates-Lorilleux, were different rosin-modified phenolic resins. Their characteristics are summarized in Table 1. Hard resin A with low solubility characteristics is commonly used in heatset formulations, contrary to hard resin B, which is more appropriate for quickset formulations. The methyl esters derived from ROA and SOA were obtained according to a process established in the authors' laboratory (12). The isomerized methyl esters derived from SOA and the methyl esters derived from linseed oil were purchased from Robbe (Compiegne, France).

Heatset varnishes. A mixture of the calculated amount of hard resin A, alkyd resin, and diluent was placed in a four-necked reaction flask, equipped with an agitator and a thermometer. The mixture was heated to 180°C at 20°C/min under a nitrogen atmosphere. Then, dissolution was completed at 180°C for 10 min. Finally, the mixture was allowed to cool to room temperature. All heatset varnish formulations are listed in Tables 2 and 3.

Quickset varnishes. The same apparatus was used, but the mixture of hard resin B, alkyd resin, and diluent was only dispersed at 150°C under a nitrogen atmosphere for 10 min before it was allowed to cool to room temperature. The varnishes formulated are shown in Table 4.

Each heatset or quickset formulation that used mineral oils as diluent, whatever the alkyd resin used, had composition similar to the two standard varnishes A1-L1 and B1-L1 (Tables 2, 4). A standard was used to adjust the methyl ester content in order to obtain varnishes with the appropriate viscosities from vegetable–diluent-based varnishes. Inks formulated with these varnishes were printed on a Favorit Man Roland press, equipped with a drier system for heatset printing.

Varnish and ink characterization. Laray viscosities, expressed in Poises-Laray, were determined at 23°C (ambient temperature), with a Falling Rod Laray Viscosimeter (Model VM. 01; Adamel Lhomargy, Ivry/Seine, France) according to TEC 003/03M procedure (Coates-Lorilleux-Total, Thourotte, France). A glass rod was used with fluid samples, and a steel rod was used with viscous samples. Tack values were measured with a Tack-o-scope tackmeter (Rudolph Meyer) at 30°C. Operating conditions were sample volume (measured with an IGT pipette), 0.6 cm^3; test speed, 100 m/min; distribution time, 1 min. Heptane tolerances were obtained according to the TEC 003/09M procedure (Coates-Lorilleux-Total).

TABLE 3
Formulations of the Heatset Varnishes with Fatty Esters as Diluent (per 100 g)

Varnish	A2-L1/R	A2-L1/S	A2-R1 (R1 Alkyd) A2-R2 (R2 Alkyd) A2-R3 (R3 Alkyd)	A2-S1 (S1 Alkyd) A2-S2 (S2 Alkyd) A2-S3 (S3 Alkyd)	A2-R3/1 (Alkyd R3)	A2-S2/1 (Alkyd S2)	A3-S2 (Alkyd S2)	A4-S2 (Alkyd S2)
Resin A (g)	46	46	47	47	45.5	45.5	47	43
Alkyd L1 (g)	16.5	16.5	—	—	—	—	—	—
Rapeseed alkyd (g)	—	—	17	—	16.5	—	—	—
Sunflower alkyd (g)	—	—	—	17	—	16.5	17	16
Rapeseed esters (g)	37.5		36	—	38	—	—	—
Sunflower esters (g)	—	37.5	—	36	—	38	—	—
Linseed esters (g)	—	—	—	—	—	—	36	—
Isomerized esters (g)	—	—	—	—	—	—	—	41

TABLE 4
Formulations of the Quickset Varnishes (per 100 g)

Varnish	B1-L2	B1-R4	B1-S4	B2-L2/R	B2-L2/S
Resin B (g)	38	38	38	44	44
Alkyd L2 (g)	24	—	—	26	26
Alkyd R4 (g)	—	24	—	—	—
Alkyd S4 (g)	—	—	24	—	—
Mineral oil 280–310°C (g)	36	36	36	—	—
Tridecanol (g)	2	1	1	—	—
Rapeseed esters (g)	—	—	—	30	—
Sunflower esters (g)	—	—	—	—	30

RESULTS AND DISCUSSION

Replacement of linseed oil-based alkyds by ROA and SOA. Heatset varnishes. A series of varnishes for heatset printing, varnishes “A1,” based on ROA or SOA and a hard resin, resin “A,” was first prepared according to the formulations shown in Table 2. After dissolving, the cloudy varnishes revealed a lack of resin solubility (Table 5). The clear varnishes must behave in accord with the specifications, corresponding to the characteristics of the standard varnish A1-L1, listed in Table 5. Only the two varnishes A1-R3 and A1-S3 that contained the longer alkyd resins were clear. This indicated that there is a limit to the oil length for dissolving, and alkyds that are too short are insoluble in this type of varnish. The solvent power effect can explain the shorter alkyds lack of solubility. The hydrocarbon aprotic apolar solvents defavor chemical interactions between the hard resin molecules and the alkyd resin molecules that associated or folded up when diluted in a poor solvent (13–15). These are two properties linked to the oil content (11). Secondly, specific interactions between the two types of resins, involving the alkyd fatty chains, can also explain the insolubility of the shorter alkyds. According to this last hypothesis, the lack of solubility of the four shorter alkyds can be attributed to a lack of interactions caused by the decrease of fatty chain content of this kind of alkyd.

A1-R3 and A1-S3 varnishes were characterized by lower viscosities than the reference varnish A1-L1 because of the lower viscosities of the alkyds R3 and S3 (11). The heptane tolerances of the two formulated varnishes A1-R3 and A1-S3, shown in Table 5, were similar to the reference, and no effect of the alkyd nature on solvent tolerance can be noticed.

Tack studies permit an evaluation of the stability and drying rate of the varnishes on a system that reproduces presswork conditions. The tack kinetics, shown in Figure 1, are characteristic of a drying mechanism that associates evaporation of the liquid fraction and oxydopolymerization of the resinous part. The tack increase, in the first step, is attributed to evaporation of the mineral oils and produces an increase of viscosity. When most of the liquid fraction is evaporated, the viscosity reaches a maximum that corresponds to the maximum tack value (Tack_m). The oxidative drying is shown, in a second step, by a tack decrease. This results in most drying varnishes reaching the maximum tack value in a shorter time.

Substitution of the alkyd L1 by alkyds R3 and S3 resulted in higher tack values than the standard despite lower varnish viscosities. Then, the two varnishes, A1-R3 and A1-S3, showed less drying (Fig. 1, Table 5). The two varnishes tested are more cohesive than the reference B1-L1. The ROA- and SOA-based alkyds R3 and S3 contain lower- molecular-weight species than the linseed oil-based alkyd L1, can interact more easily with the other varnish components and increase the internal cohesion of the mixtures (11). Consequently, the resulting tack values are higher, and the drying achievements are weaker.

Since A1-R3 and A1-S3 varnishes reached all required specifications, the ink formulations were prepared. These inks were characterized before printing on a pilot heatset press. Only red inks were formulated. The two formulated red inks, A1-R3 and A1-S3, showed similar characteristics to the reference ink A1-L1. The press behavior of the inks was good, and the corresponding prints reached the required quality level.

Quickset varnishes. ROA and SOA were also evaluated in varnishes for sheet-fed printing, which requires a larger pro-

TABLE 5
Characteristics of the Heatset Varnishes A1 with Mineral Oil as Diluent

	Standard	ROA-based varnishes			SOA-based varnishes		
Varnish	A1-L1	A1-R1	A1-R2	A1-R3	A1-S1	A1-S2	A1-S3
Solubility	C	T	T	C	T	T	C
Viscosity at 23°C (Poises-Laray)	320	—	—	250	—	—	238
Heptane value (cm^3)	55	—	—	54	—	—	54
Tack_m value	120	—	—	130	—	—	127

Abbreviations: C: clear; T: turbid.

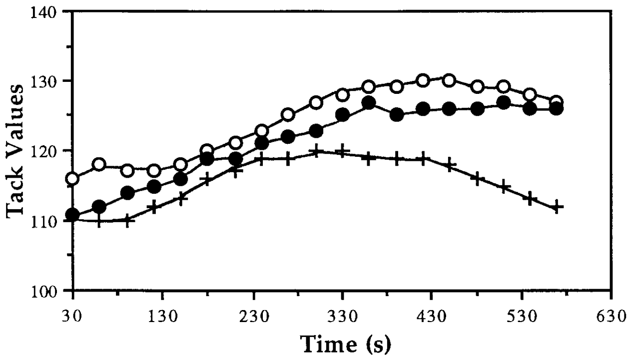

FIG. 1. Tack values of the A1 heatset varnishes with a mineral oil as diluent; ○, A1-R3; ●, A1-S3; +, A1-L1 (REF.).

portion of alkyd resin due to the prominent oxidative drying mechanism. Adjustment of the oil length was necessary to obtain appropriate viscosities of ROA and SOA for sheet-fed applications. The two alkyds obtained contained 64% vegetable oil and were marked R4 and S4 (Table 6). The corresponding varnishes, based on hard resin B, were marked B1-R4 and B1-S4 (Table 4). These two varnishes were formulated at 99% to obtain accurate viscosities.

Much like the heatset varnishes, the substitution of linseed oil-based alkyd L2 by ROA or SOA resulted in more cohesive varnishes. This was revealed by higher tack values (Table 7). Blue inks and yellow inks were formulated with these three varnishes. A 1% increase of the dry extract for the blue ink, and a 1.5% increase for the yellow ink, were required to obtain accurate viscosities for formulations composed with rapeseed oil-modified alkyd R4. Finally, quadrichrom printing attempts were carried out with industrial red and black ink; all subsequent tests carried out on the dry prints were satisfactory. No difference between the standard inks and the test inks could be observed.

The longer alkyds, R3 and S3, and the intermediate alkyds, R4 and S4, have the required properties for heatset printing and sheet-fed printing, respectively. Their use does not demand any modification of established formulations. If some disparities were noticed between ROA and SOA on alkyd molecular structures and properties, the fatty acid composition of the modifying vegetable oil seems to have no influence on varnish characteristics, ink behavior on the press, and the visual quality of the resulting prints. Furthermore, the drying abilities were similar to the reference inks, and the lack of drying of the ROA and SOA had no effect on drying properties of the printed inks.

TABLE 6
Characteristics of the Alkyds R4 and S4 for Quickset Formulations

	Sunflower oil	Rapeseed oil	Linseed oil
Alkyd	S4	R4	L2
Oil length (%)	64	64	72
Viscosity-23°C (Poises-Laray)	100	135	125

TABLE 7
Characteristics of the Quickset Varnishes B1 with Mineral Oils as Diluent

	Standard varnish	ROA-based varnish	SOA-based varnish
Varnish	B1-L2	B1-R4	B1-S4
Solubility	C	C	C
Viscosity at 23°C (Poises-Laray)	400	440	330
Tack$_m$ value	250	290	280

Abbreviation: C: clear.

Substitution of the mineral oil fraction by methyl esters derived from vegetable oils. Quickset varnishes. Replacement of hydrocarbon solvents with methyl esters derived from ROA and SOA was first carried out in quickset varnishes, that require a less volatile liquid fraction than heatset formulations. The fatty acid composition effects of each vegetable oil-derived diluent on varnish properties were studied. The varnish called B2-L2/R was composed of rapeseed esters, and the varnish called B2-L2/S was based on sunflower esters (Table 4). These two varnishes were perfectly clear, but a 8% increase of the dry extract was necessary to reach the specified viscosity, showing the high diluting power of these vegetable diluents (Table 3). Tack behavior was modified, as shown in Figure 2, and revealed new drying properties for this new type of offset varnish. First, the regular decrease of tack kinetics reveals an absence or weak evaporation of the liquid fraction. Second, higher tack values than the standard varnish were noticed. This is due to the strong solvent power of the reactive fatty esters in comparison with the nonreactive mineral oils. The tack values increase, so the internal cohesiveness of the varnish is linked to the fatty acid composition of the esters. The varnish B2-L2/S, based on higher unsaturated fatty acid content of the ester fraction, is the more cohesive varnish because of its higher tack value. An increase in the unsaturated fatty chain content results in more solvated resins by these vegetable derivatives (SOA being composed of 62% unsaturated fatty chains vs. 33% for ROA).

Only varnish B2-L2/S, having more suitable tack values,

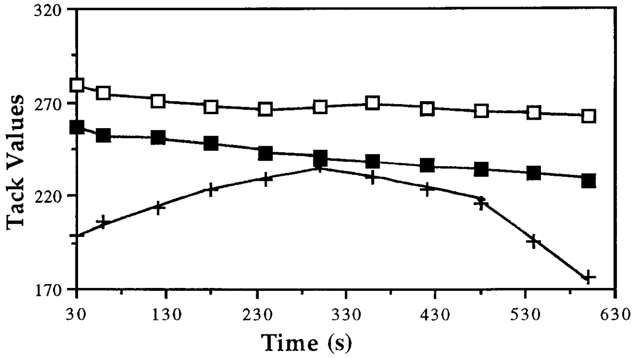

FIG. 2. Tack values of the B2 quickset varnishes with methyl fatty esters as diluent; □, B2-L2/R; ■, B2-L2/S; +, B1-L2 (REF.).

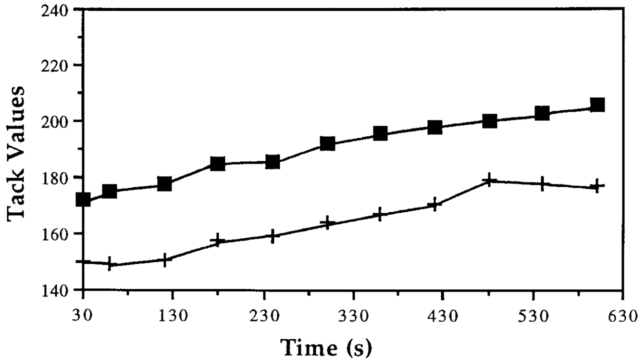

FIG. 3. Tack values of the quickset inks; ■, B2-L2/S; +, B1-L2 (REF.).

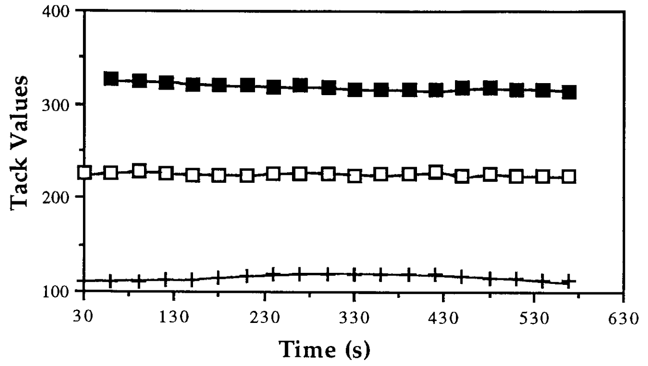

FIG. 4. Tack values of the A2 heatset varnishes methyl fatty esters as diluent; □, A2-L1/R; ■, A2-L1/S; +, A1-L1 (REF.).

was pigmented. The red ink obtained from B2-L2/S showed higher tack values than the standard ink, but they were insufficient to forbid sheet-fed press tests (Fig. 3). The press behaviors of the red ink tested were satisfactory and exceeded the standard for some characteristics. Press cleaning was made easier by use of the fatty esters. The corresponding prints had desirable qualities. The methyl esters derived from vegetable oil, particularly from SOA, seem to be adapted to sheet-fed printing; the ink produced with this vegetable diluent dries as quickly as the traditional ink. However, subsequent tests, on a longer production cycle, must now be realized to confirm the good press behavior of the vegetable-based ink and the absence of postprinting defects of the prints.

Heatset varnishes. Two heatset varnishes, according to the same approach, A2-L1/R (rapeseed esters) and A2-L1/S (sunflower esters), were prepared and evaluated (Tables 5, 8). A 9.5% increase of the dry extract was necessary to obtain suitable viscosities, revealing a higher diluting power of the esters in this kind of varnish. Use of the methyl esters resulted in higher heptane tolerances (Table 8), and the modified tack behaviors were similar to the quickset varnishes as shown in Figure 4. Tack values of the vegetable-based varnishes are again higher than the standard A1-L1, and the tack value increase is linked to the fatty acid composition of the esters.

However, with the two formulated varnishes having tack values that were too strong, the following step was not carried out. The fatty esters that result in tack values being too strong and some important modifications of the drying properties cannot be used as such, in the actual heatset formulations. Strong tack reveals strong cohesivity, and presumably, leads to bad press behavior, particularly on a web press operating at high rates with delicate paper. Finally, absence or weak evaporation of the liquid fraction certainly has a negative effect on heatset printing.

TABLE 8
Characteristics of the Heatset Varnishes A2-L1 with Methylic Esters as Diluent

	Standard	Sunflower esters	Rapeseed esters
Varnish	A1-L1	A2-L1/S	A2-L1/R
Solubility	C	C	C
Viscosity at 23°C (Poises-Laray)	320	315	325
Heptane value (cm^3)	54	79	79

Abbreviation: C: Clear.

Formulations associating methyl esters derived from vegetable oils with ROA and SOA. The ROA and SOA have different properties than the usual alkyd resins, and some formulation attempts based on their methyl esters were carried out to yield usable "green" heatset inks. Six formulations, based on R1, R2, R3, S1, S2, and S3 alkyds, were prepared according to the procedures shown in Table 3. Substitution of the petroleum products by the vegetable diluents permitted solubilization of all oleoglycerophtalic alkyds (Table 9). In varnishes based on a vegetable-derived diluent, the alkyd molecules cannot be easily associated or folded because of the strong solvent power of the fatty esters. So, the alkyd molecules, free and stretched, can interact more easily with the hard resin and, consequently, are more soluble. More interactions between ester and alkyd fatty chains can also explain the homogeneous mixtures obtained.

The use of fatty esters to substitute for mineral oil again resulted in an important viscosity decrease when standard procedures were used. An 11% increase of the dry extract was required to obtain suitable viscosities, and the heptane tolerance was always higher than the reference varnish (Tables 3,9).

The tack kinetics and drying properties, as shown in Figure 5, are typical of fatty esters-based varnishes. As before, the varnishes show higher tack values than the standard varnish due to the stronger solvent power of the esters. However, the fatty acid composition of the ester mixture seems to have no effect on tack values. So, the ester composition can have an effect on varnish properties according to the alkyd's nature. Finally, the modified drying properties and the strong internal cohesiveness in this type of varnish are not suitable for successful heatset printing; therefore, varnish pigmentation for printing tests was not attempted.

TABLE 9
Characteristics of the Heatset Varnishes A2 Associating Methylic Esters with ROA and SOA

	Standard	Rapeseed varnishes			Sunflower varnishes		
Varnish	A1-L1	A1-R1	A1-R2	A1-R3	A1-S1	A1-S2	A1-S3
Solubility	C	C	C	C	C	C	C
Viscosity at 23°C (Poises-Laray)	320	380	355	325	360	365	320
Heptane value (cm^3)	54	79	74	76	79	74	82

Abbreviation: C: clear.

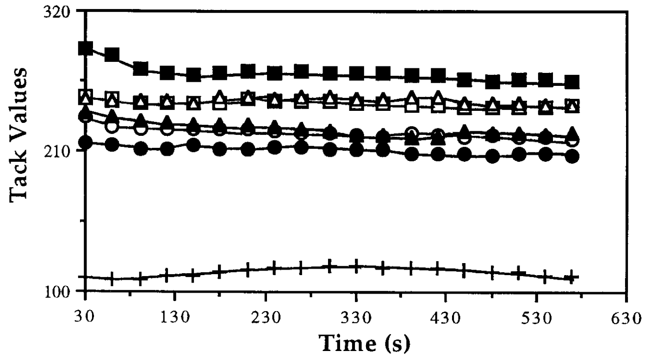

FIG. 5. Tack values of heatset varnishes associating ROA and SOA with methyl fatty esters; □, A2-R1; △, A2-R2; ○, A2-R3; ■, A2-S1; ▲, A2-S2; ●, A2-S3; +, A1-L1 (Reference).

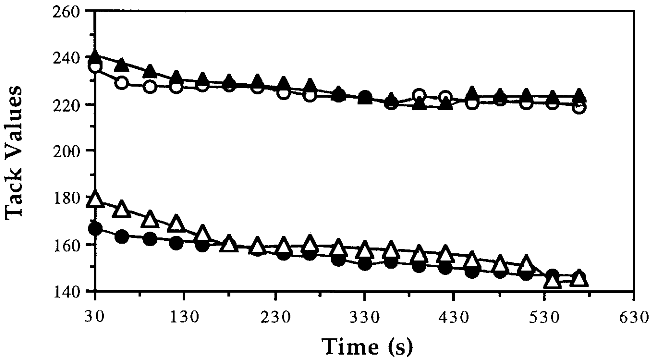

FIG. 6. Influence of the ester content on the tack values of heatset varnishes; ○, A2-R3; ●, A2-R3/1; ▲, A2-S2; △, A2-S2/1.

A 2% increase in the fatty ester content was attempted to limit the modifications caused by the use of this kind of diluent. The formulations obtained (A2-R3/1, A2-S2/1) are summarized in Table 3. The characteristics of the two varnishes formulated are listed in Table 10, and compared with the characteristics of varnishes A2-R3 and A2-S2. A small decrease of the dry extract (2%) resulted in a strong tack decrease (Fig. 6), but was associated with an important decrease in viscosity. It is not possible to increase the ester content of these formulations to obtain a good tack–viscosity balance.

Fatty acid methyl esters derived from linseed oil were used to study the influence of an increase in unsaturated fatty chain content of the diluent on these varnish properties. Isomerized fatty esters derived from SOA were introduced to evaluate the influence of the reactivity of the fatty chains. The two formulated varnishes shown in Table 3 were clear. An 11% increase of the dry extract was required, to obtain the necessary viscosity for the varnish composed of the linseed esters (varnish A3-S2), (Table 11). Only a 6% increase was necessary to yield an appropriate viscosity for the varnish A4-S2 that is based on the isomerized esters. During the dissolution process that is carried out at high temperature, the highly reactive conjugated bonds of the isomerized fatty chains can react with other unsaturated bonds to form polymers. Consequently, when the fatty chains are more reactive, a higher ester content is required to obtain the specified viscosity. In each case, the heptane values are higher than the standard value. No effect was noticed from the unsaturated fatty chain content of the diluent on heptane tolerance and tack value (Table 11). Finally, the tack kinetics, and thus the drying properties and cohesiveness, are characteristic of ester-based varnishes (Fig. 7).

Whatever the nature of the associated alkyd, fatty esters are unsuitable for heatset varnishes. Although some properties were exceeded by an increase of the fatty ester content, or by the use of more reactive esters, the lost drying charac-

TABLE 10
Influence of the Ester Content on the Characteristics of Heatset Varnishes

	Rapeseed varnishes		Sunflower varnishes	
Varnish	A2-R3	A2-R3/1	A2-S2	A2-S2/1
Viscosity at 23°C (Poises-Laray)	295	140	292	153
Heptane value (cm^3)	73	76	82	70

TABLE 11
Characteristics of Heatset Varnishes A2, A3, and A4

	Sunflower esters	Linseed esters	Isomerized esters
Varnish	A2-S2	A3-S2	A4-S2
Viscosity at 23°C (Poises-Laray)	292	285	265
Heptane value (cm^3)	82	71	71

Abbreviation: C: Clear.

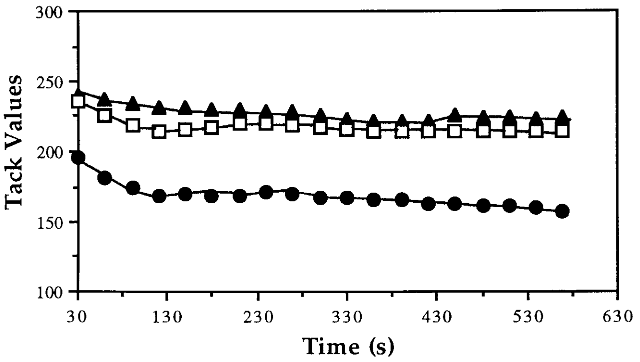

FIG. 7. Influence of the esters' nature on the tack values of heatset varnishes; ▲, A2-S2; □, A3-S2; ●, A4-T2.

teristics can not be recovered. The substitution of mineral oils in heatset varnishes requires a complete modification of the actual formulation, so the search of more adapted resins continues.

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