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Effects of drying on ASA esterification and sizing

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ABSTRACT

Sizing with alkenyl succinic anhydride (ASA) functions by forming esters with cellulose. The hydrolysis product of ASA is not an active sizing agent. The sizing level and esterification reaction are strongly influenced by drying conditions. Drying at higher temperatures has a beneficial effect on sizing and increases the rate of esterification. Prolonged drying increases sizing, but excessive drying periods may cause sizing to decrease. Conditioning ASA-treated sheets at room temperature yields higher sizing levels; both ASA esterification and hydrolysis continue after drying.

The feature that most distinguishes alkaline sizes such as alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA) from the traditional rosin-alum system is their reported ability to covalently react with cellulosic hydroxyl groups to form esters (1). The rosin-alum system, in contrast, is dependent on ionic interactions (2).

Anhydrides are known to react with alcohols, ammonia and amines, and water; the reaction being acid, or base catalyzed (3,4). ASA in a papermaking system would have two primary products as shown in Fig. 1: 1) ester-acids formed with cellulosic hydroxyl groups and 2) the di-acid hydrolysis product formed with water. Further, the organic salt could be formed preferentially to the carboxylic acid, depending on the alkalinity during sheet formation.

(Fig. 1 here)

Recent reports suggest that esterification reactions in the AKD system are unnecessary to achieve sizing, or do not occur (5-8). Other reports suggest that esterification does occur and is the primary route to sizing (9-11).

An investigation of the potential for esterification in the ASA system was stimulated by the question of reactivity in the AKD system.

The objective of the study was to determine whether ASA forms esters with cellulose that promote sizing. Additionally, the influence of the extent and rate of drying on the sizing level and ASA reaction was studied.

Examination for the ester

To determine whether an ester was formed between cellulose and ASA under very favorable conditions, a cotton linters pulp was reacted with a commercial ASA in N,N-dimethylformamide with triethylamine as a catalyst.

The major infrared (IR) peaks due to ASA carbonyl stretching are located at approximately 1782 and 1865 cm^{-1} . An ester formed between cellulose and ASA should display a peak due to carbonyl stretching between 1735 and 1750 cm^{-1} (12). As shown in Fig. 2, ASA produces no IR bands in the ester range. The carbonyl stretching of the acid group formed during hydrolysis, or in conjunction with esterification, was determined to appear at approximately 1710 cm^{-1} . Organic salts of the carboxylic acid were found to display peaks at approximately 1405, 1450, and 1570 cm^{-1} .

(Fig. 2 here)

A diffuse reflectance IR peak, as shown in Fig. 3, at approximately 1732 cm^{-1} was taken as evidence of ASA esterification with cellulose in the system described above.

(Fig. 3 here)

The study was then extended to determine whether esterification of ASA with cellulose was also possible under papermaking conditions. Preliminary examinations showed that ASA could react with both the starch and the activator supplied with the ASA. Since it was desirable to have the ASA react only with cellulose, a nonreactive, cationic polymer, poly(1,2-dimethyl-5-vinylpyridinium bromide) (DMVPB), was substituted as a retention aid. As shown in Fig. 4, DMVPB produces no IR peaks in the ester range. Additionally, ASA emulsification was performed using shearing in distilled water without any activator. The components of the sheet were thus: 1) cotton linters, 2) ASA, 3) DMVPB, and 4) sodium hydroxide and sulfuric acid to control pH.

(Fig. 4 here)

IR examination of oven dried sheets by diffuse reflectance provided indications of retained ASA, formation of the ester, and formation of acid groups resulting from ester formation or ASA hydrolysis. The IR ester bond was evident in ASA sheets upon subtraction of the spectrum of a pure cotton linters sheet from the ASA sheets. As shown in Fig. 5, the acid and ester peaks appear as mutual shoulders at 1714 and 1732 cm^{-1} , respectively. Residual ASA is apparent at 1785 and 1865 cm^{-1} .

(Fig. 5 here)

Effects of drying on the level of sizing

Sizing levels were tested with a Hercules Sizing Tester under conditions of varied drying temperature, drying time, and conditioning time. Typical sizing results are shown in Fig. 6. The sizing levels increased as drying times increased and were greater at a particular drying time when the temperature was increased. Further, higher drying temperatures yielded higher size test maxima. At the longer drying times the sizing was found to decrease. The extent and the rate of the decrease was variable.

(Fig. 6 here)

In Fig. 7, the only conclusive effect of conditioning sheets prior to testing the sizing level was that conditioned sheets displayed greater sizing at short drying times when compared with unconditioned sheets. This could logically be related to unreacted ASA forming esters during conditioning.

(Fig. 7 here)

In other experiments not shown here, no conclusive differences could be observed between sheets conditioned one day and those conditioned one week before testing the sizing level.

To determine whether the ASA hydrolysis product was a sizing agent, sheets were formed with the hydrolysis product, as shown in Table 1, in a manner similar to that used with sheets containing ASA. DMVPB or alum was also added. Retention of the hydrolysis product, as measured by its IR peak, was poor relative to that of ASA, and the sheets displayed no sizing using 1% formic acid ink and a 65% reflectance endpoint. To increase hydrolysis product retention, sheets were formed at higher consistencies (1-2%), using 1-43% hydrolysis product addition levels. Sheets were made using 1) only the ASA hydrolysis product or 2) the ASA hydrolysis product and 0.15% DMVPB. Retention was improved, as the IR peak of the hydrolysis product was quite evident. These "high consistency" sheets also displayed no sizing using 1% formic acid ink and a 65% reflectance endpoint. Sheets formed at similar high consistencies with 0.25% ASA displayed strong sizing (800 seconds) using 10% formic acid ink and a 90% reflectance endpoint.

(Table 1 here)

Sheets were also formed with 0.5% ASA, stored in plastic wrap one week, and then pressed and dried. These sheets displayed significantly lower sizing levels (70 seconds using 1% formic acid ink and a 65% reflectance endpoint) than sheets formed with ASA that were pressed and dried immediately after formation (800+ seconds using 10% formic acid ink and a 90% reflectance endpoint). Delaying the pressing and drying of a sheet should yield increased hydrolysis product levels.

The above results suggest the ester formed in the ASA system is the main promoter of sizing, rather than the ASA hydrolysis product.

ASA reaction in the sheet

The ASA reaction in the sheet was examined by forming sheets with greater than usual levels of ASA (1.5%) to make the results visible by spectroscopy. Sheets

were then examined by diffuse reflectance IR for relevant peaks and their variation with conditioning, drying time, and drying temperature. Subtractive methods were used. This yielded a semiquantitative measurement of the materials contained in the sheet.

A sequence of events was found to occur within one week of sheet formation. The extent to which each event occurs and the rate at which it occurs is dependent on the drying temperature, the drying time, and the time of examination. The sequence is: 1) during drying, ASA is consumed to form esters with cellulose or the hydrolysis product with water; the ASA may also volatilize off the sheet, 2) during conditioning, more ASA is consumed, and additional esters and hydrolysis product are formed, and 3) after one week of conditioning, the ASA is fully consumed (as measured by IR examination of the sheet); the acid peak decreases and the ester peak increases relative to the levels after one day of conditioning.

In Fig. 8, ester development with drying time at several drying temperatures is shown. Increases in temperature lead to faster ester development. Ester formation appears to stabilize after about 60 minutes at 105°C, and after longer times at the lower temperatures.

(Fig. 8 here)

Figure 9 suggests that excess ASA may volatilize during drying. The products (ester and acid) appear to reach a maximum after 60 minutes, but the ASA continues to decrease after that time.

(Fig. 9 here)

Sheets extracted with toluene immediately after drying displayed decreases in the ester-acid peak. A variation in the acid or ester will cause a variation

in the other because they are mutual shoulders. Since the ester would not be extractable, the decrease must be due to hydrolysis product removal. This suggests the hydrolysis product is formed with the ester during drying.

In Fig. 10, sheets conditioned for one day show increases in the ester and the acid compared with unconditioned sheets. The greatest increase after one day is in the acid peak, suggesting that ASA remaining after drying readily yields the hydrolysis product. This may be concluded, since the acid peak becomes noticeably larger than the ester peak during conditioning at the shorter drying times - a reverse of the situation in the unconditioned sheets. At shorter drying times there would be more residual ASA present than at longer drying times. Additionally, the shorter drying times display the greatest acid increases after conditioning for one day.

(Fig. 10 here)

After one week of conditioning the acid peak has decreased, as shown in Fig. 10. This also causes the ester measurement to decrease because the acid and ester peaks are mutual shoulders. The decrease in the acid peak may be due to vaporization, but a peak simultaneously forming at about 1576 cm^{-1} suggests the acid is involved in an unexpected side reaction. Additionally, sheets extracted with toluene after one day of conditioning, when the hydrolysis product level is still high, do not display the peak development at 1576 cm^{-1} . Extraction of the sheets with toluene after several months and IR examination of the extract yielded definite evidence that the hydrolysis product was still present and that some unreacted ASA remained.

In Fig. 11, IR examination of sheets extracted with toluene to remove the hydrolysis product shows that the ester also continues to form after drying.

(Fig. 11 here)

Conclusions

ASA clearly forms esters with cellulose and promotes sizing primarily by esterification. The hydrolysis product is a poor sizing^{*} agent and could be, as suggested by others, a desizing agent (13). The rate of sizing development is dependent on the drying temperature, and the extent of sizing is dependent on the conditioning time, the drying time, and the drying temperature. Long term drying of the sheet causes sizing to decrease. Conditioning of the sheets, when unreacted ASA would be expected to be present, yields increased sizing levels.

The rate of ester formation is dependent on the drying temperature, and ester formation continues after drying. Hydrolysis of the ASA occurs during drying, and extensively after drying if ASA is available. The acid groups increased during initial conditioning and then decreased after one week. Unexpected side reactions of an undetermined nature appeared to consume the acid, but loss of the hydrolysis product through vaporization cannot be eliminated from consideration. Finally, after several months, unreacted ASA and the hydrolysis product were still present in the sheet.

Experimental procedures

The pulp used was a bleached, commercial cotton linters. The pulp was treated in a Valley Beater to 290 mL CSF and then Soxhlet extracted in 1:1 chloroform: 95% ethanol for 48 hours, washed in distilled water, air dried, and bagged.

The polymer, DMVPB, was synthesized by Eggert. The approximate weight average molecular weight is 10^6 (14).

The ASA was determined by GC/MS to be a mixture of isomers, primarily of a molecular weight of 322 g/mole. Silation of the hydrolysis product was used to obtain volatility.

The hydrolysis product was prepared by reacting ASA with a small excess of distilled water at room temperature for 3 days.

The reaction of ASA in N,N-dimethylformamide was performed at 85°C for 1.25 hours. Approximately 3.5 grams of cotton linters was mixed with 100 mL of N,N-dimethylformamide, 25 mL of ASA, and 0.3 mL of triethylamine. The reacted linters were filtered, Soxhlet extracted in toluene, and oven dried to remove residual N,N-dimethylformamide.

Emulsions of ASA or the hydrolysis product were made using distilled water in an Eberbach 8590 mixer. ASA emulsions were prepared at 1.5% ASA and used immediately to prevent hydrolysis. A new emulsion was used for each sheet.

Handsheets (1.8 O.D. grams) were made using prewetted cotton linters dispersed in a British Disintegrator. The pulp was diluted to the proper consistency (generally 1%) and adjusted to a pH of 7.5. The ASA or hydrolysis product emulsion was gently stirred with the pulp two minutes, and 0.15% DMVPB was added immediately afterward with gentle stirring for a further two minutes. The pulp was added to a British handsheet mold filled with deionized water that had been preadjusted to a pH of 7.5. Sheets were formed and pressed in accordance with TAPPI Standard T205 om-81 and oven dried in a convection oven immediately to prevent hydrolysis of the ASA. All sheets containing either ASA or the hydrolysis product were dried one hour at 105°C, unless otherwise noted. Sodium hydroxide and sulfuric acid were used for pH adjustment. Samples were conditioned at 72°F and 50% RH, unless otherwise noted.

Extraction of sheets was performed using a Soxhlet extraction apparatus with toluene for 14-18 hours.

Size tests were performed using a Hercules Sizing Tester, 10% formic acid ink, and an 80% reflectance endpoint, unless otherwise noted. Test ink was applied to the felt side of the sheet.

IR spectra were produced using a Nicolet 7199 FT-IR at 2 cm^{-1} resolution. Diffuse reflectance spectra were obtained using 500 scans in a Harrick's Praying Mantis unit mounted in the FT-IR. A potassium chloride background was used for all samples. All spectra were base line corrected from $400\text{--}4000\text{ cm}^{-1}$.

Subtractive results were obtained using a cotton linters sheet and a $1350\text{--}2000\text{ cm}^{-1}$ subtraction range. Results were base line corrected from $1685\text{--}1900\text{ cm}^{-1}$ before measuring the peak height.

Transmission spectra of extracts were obtained on sodium chloride plates using the instrument described above.

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Table 1: Compositions of sheets containing the hydrolysis product and their respective size tests.

%ASA Hydrolysis Product	% DMVPB	%Alum	Hercules Size Test (secs.)
0.5 ¹	0	0.7	0
0.5 ¹	0.15	0	0
1.0 ¹	0.15	0	0
0.5 ²	0	0.35	0
0.5 ²	0	0.7	0
0.5 ²	0.15	0	0
1.0 ²	0.15	0	0

¹Hydrolysis product added to pulp before DMVPB or alum.

²Hydrolysis product added to pulp after DMVPB or alum.

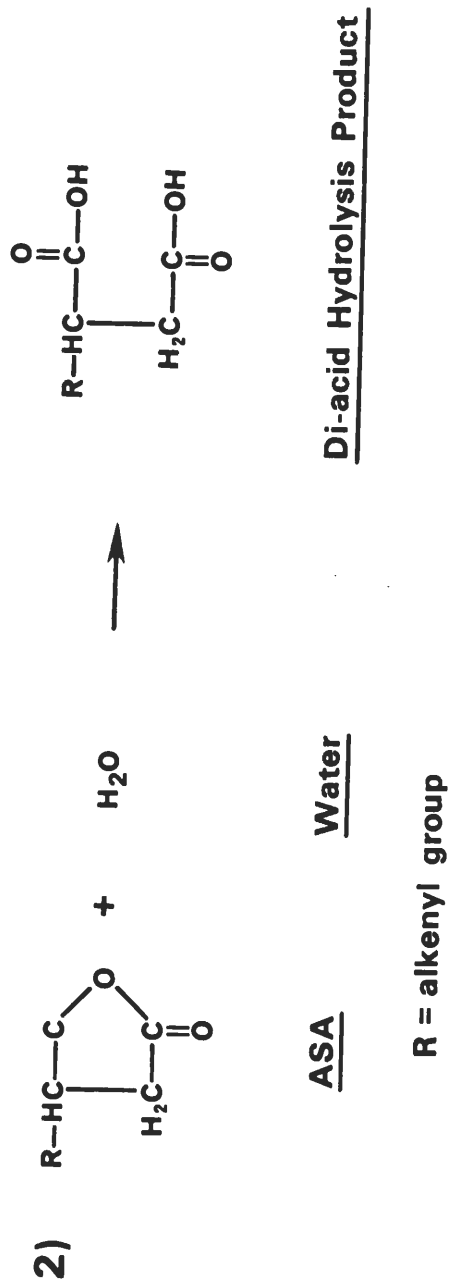
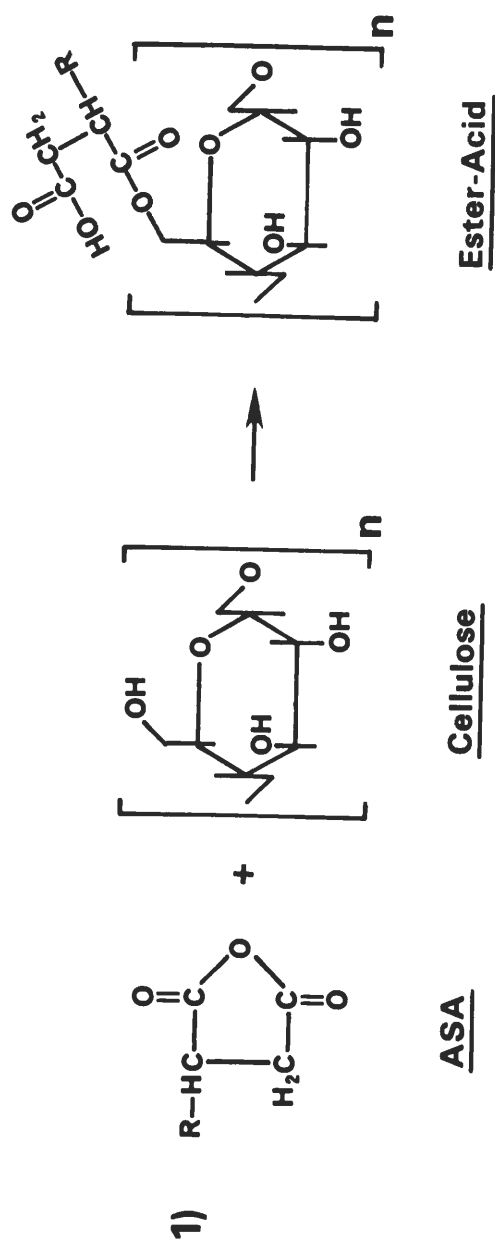


Figure 1. ASA reactions in a papermaking system.

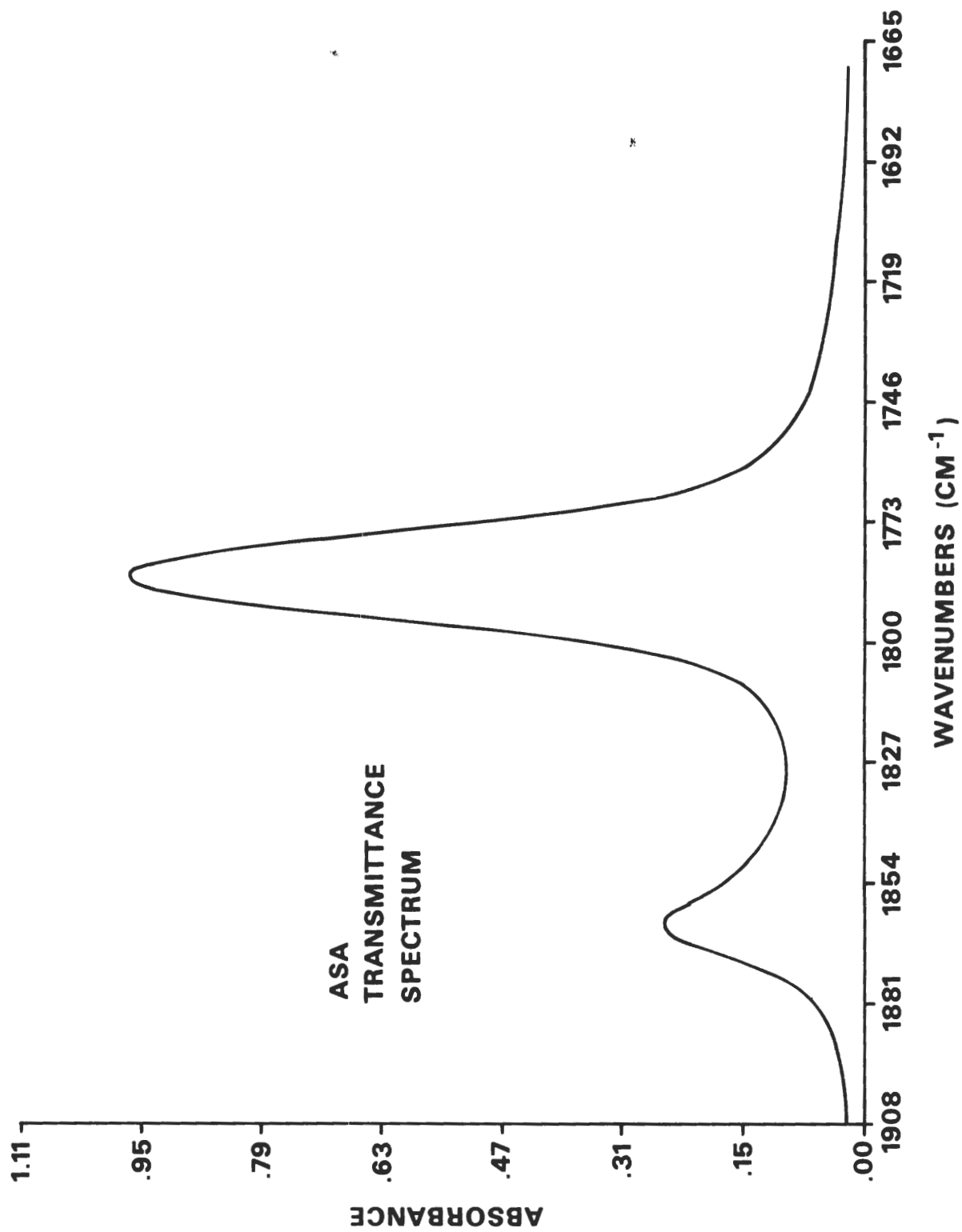


Figure 2. IR transmission spectrum of commercial ASA.

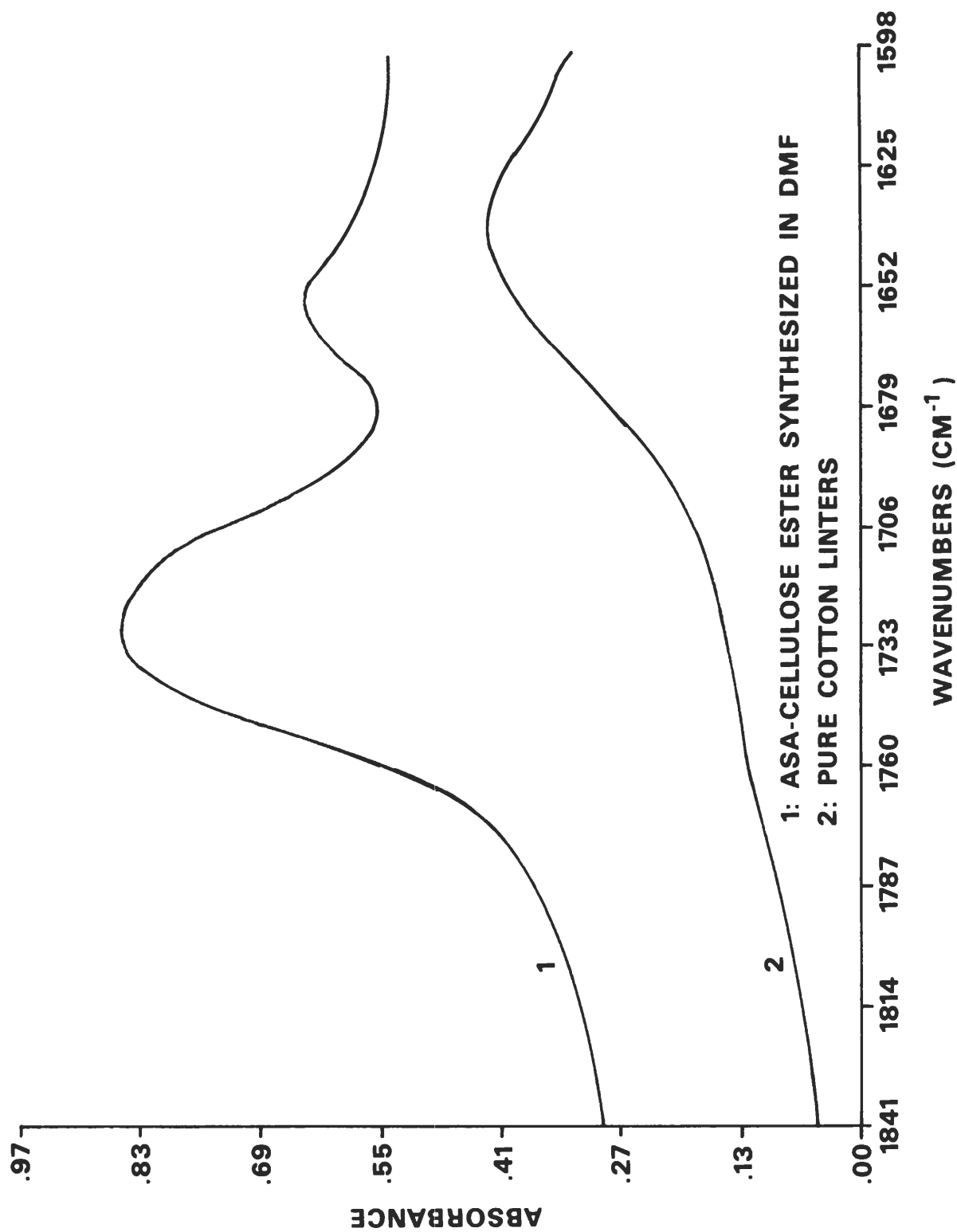


Figure 3. Diffuse reflectance IR spectra of the ASA-cellulose ester formed in DMF, and pure cotton linters before reaction.

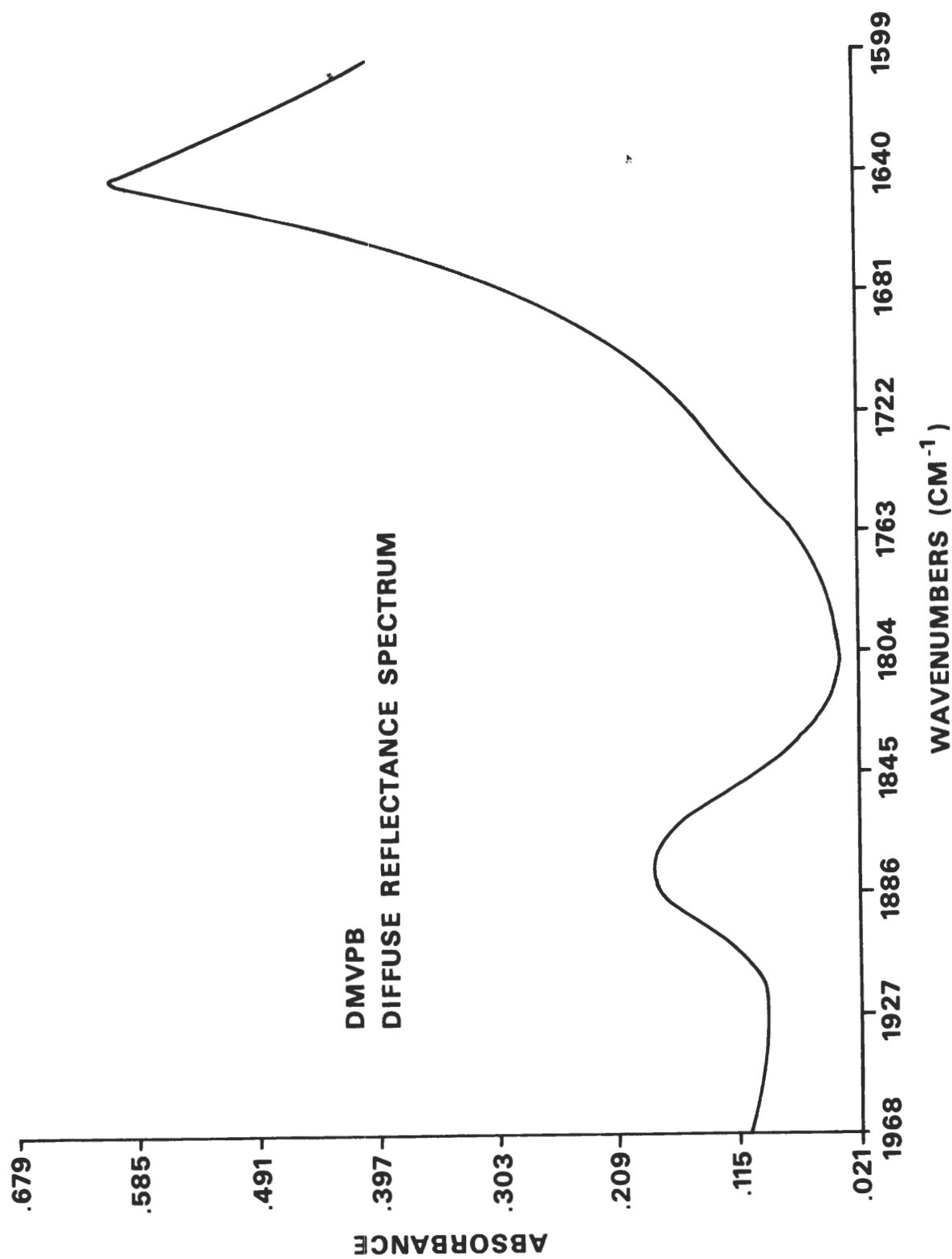


Figure 4. IR diffuse reflectance spectrum of poly(1,2-dimethyl-5-vinylpyridinium bromide).

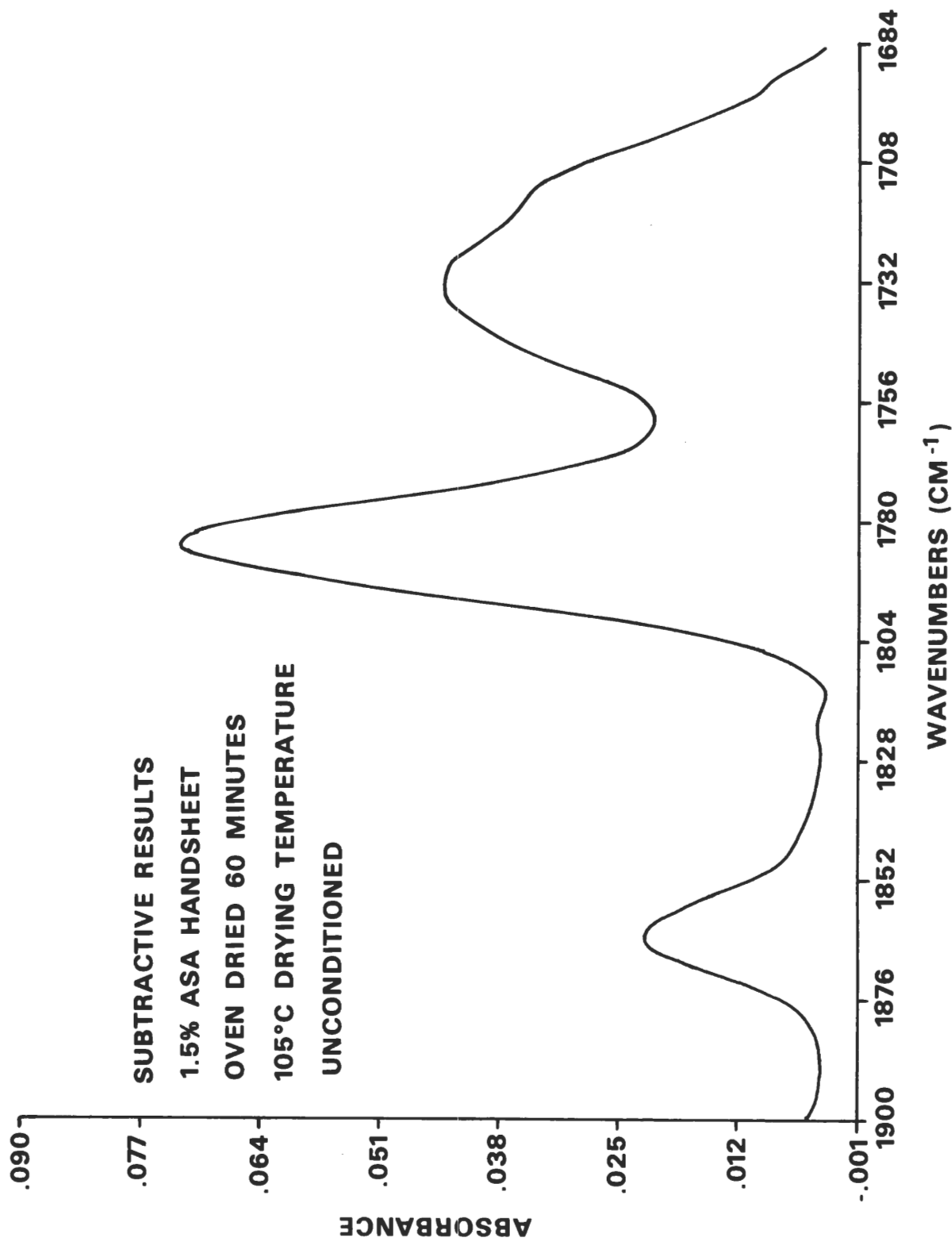


Figure 5. Diffuse reflectance IR subtraction spectrum of an ASA-containing handsheet.

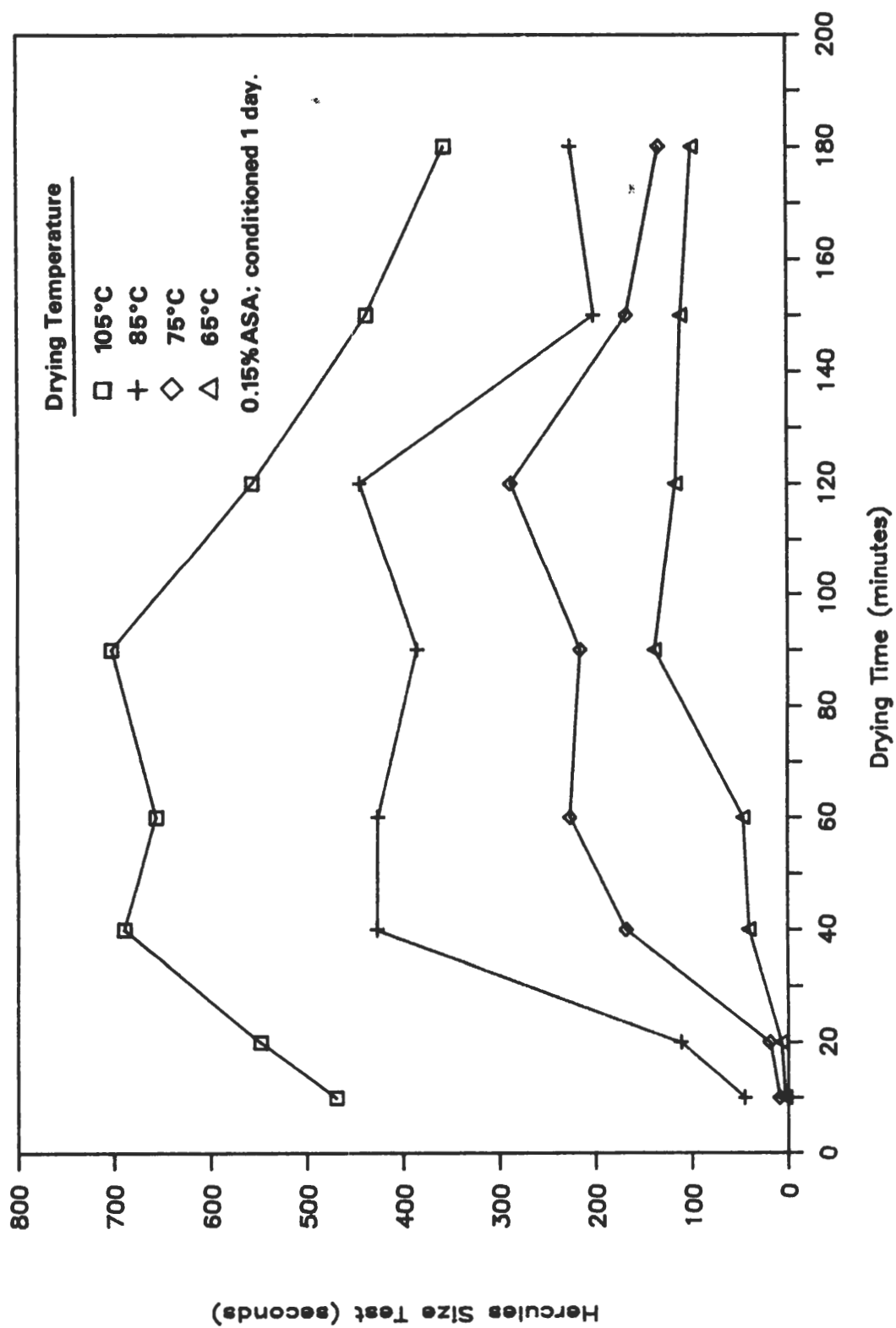


Figure 6. Development of ASA sizing at different drying temperatures.

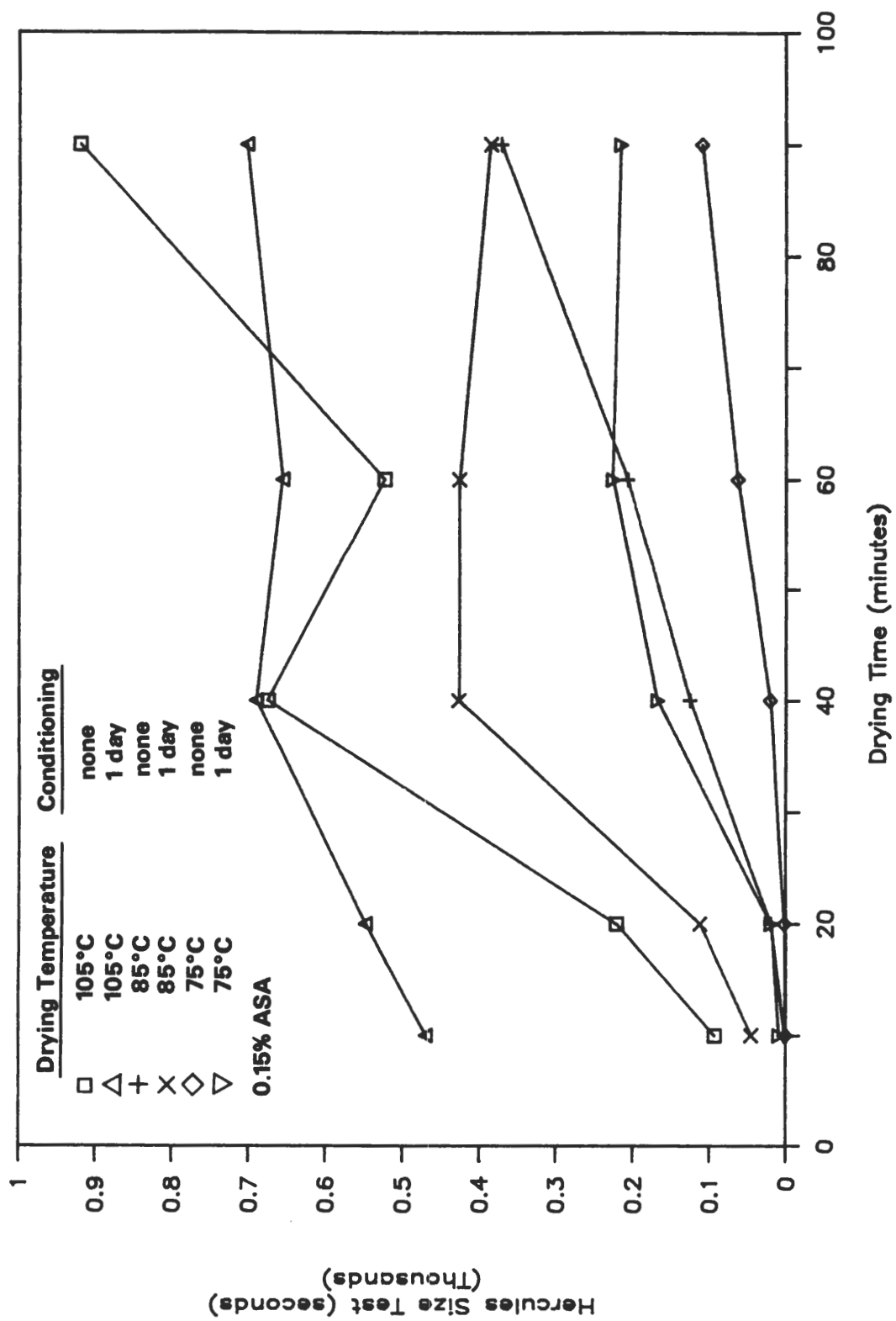


Figure 7. Development of ASA sizing at different drying temperatures during conditioning.

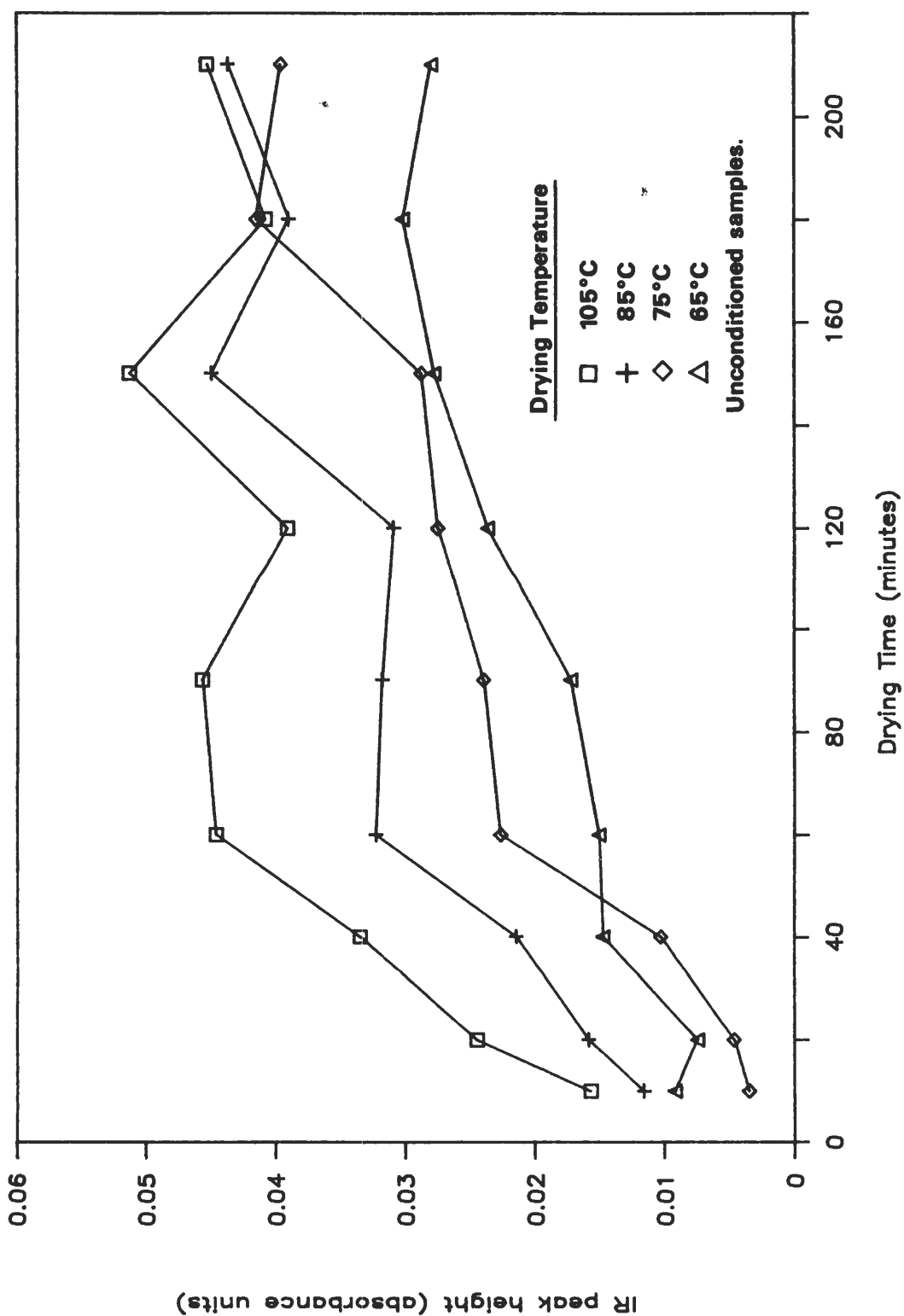


Figure 8. Development of the ester IR peak in a handsheet during drying at different drying temperatures.

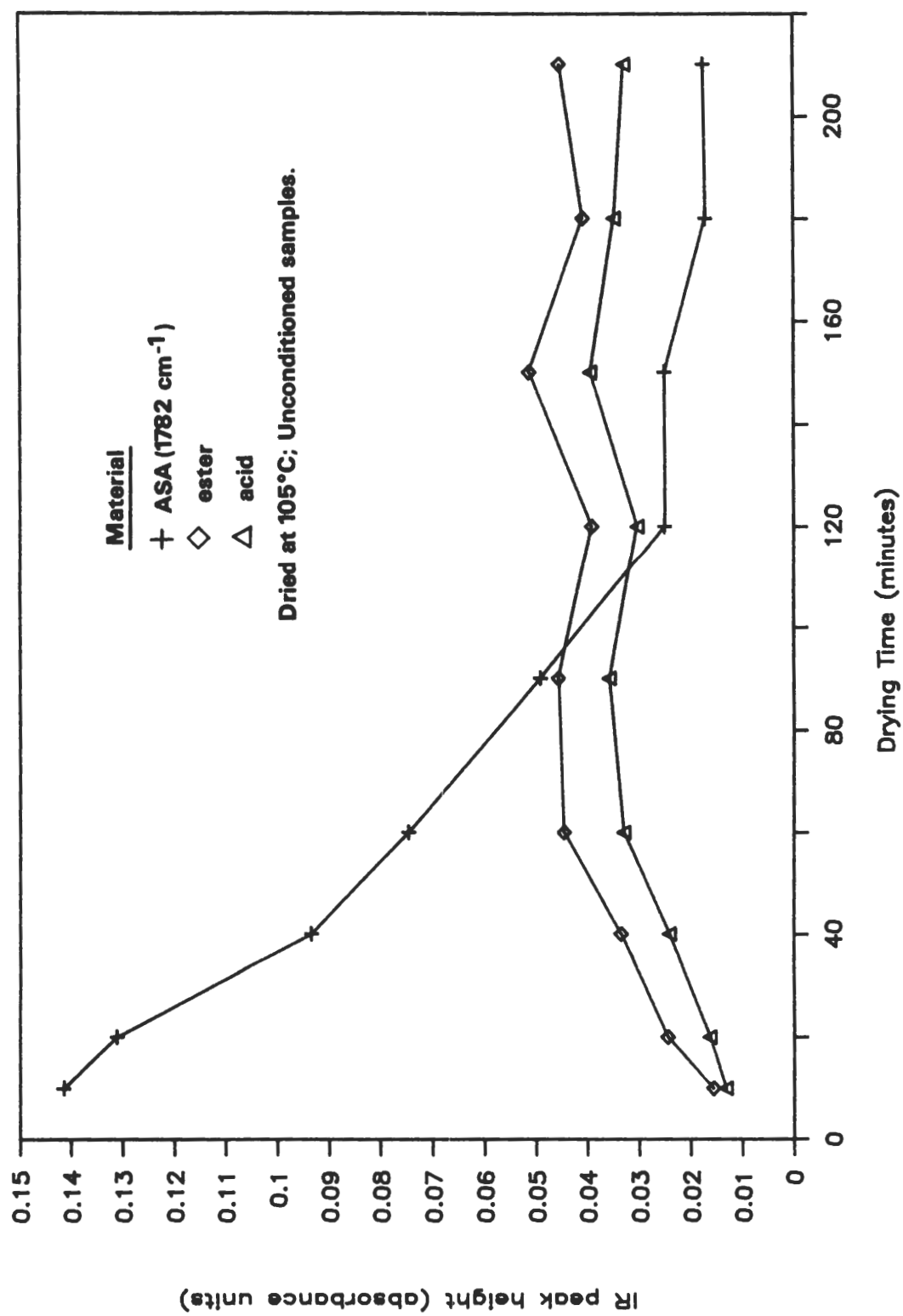


Figure 9. Variation in peak heights with drying time.

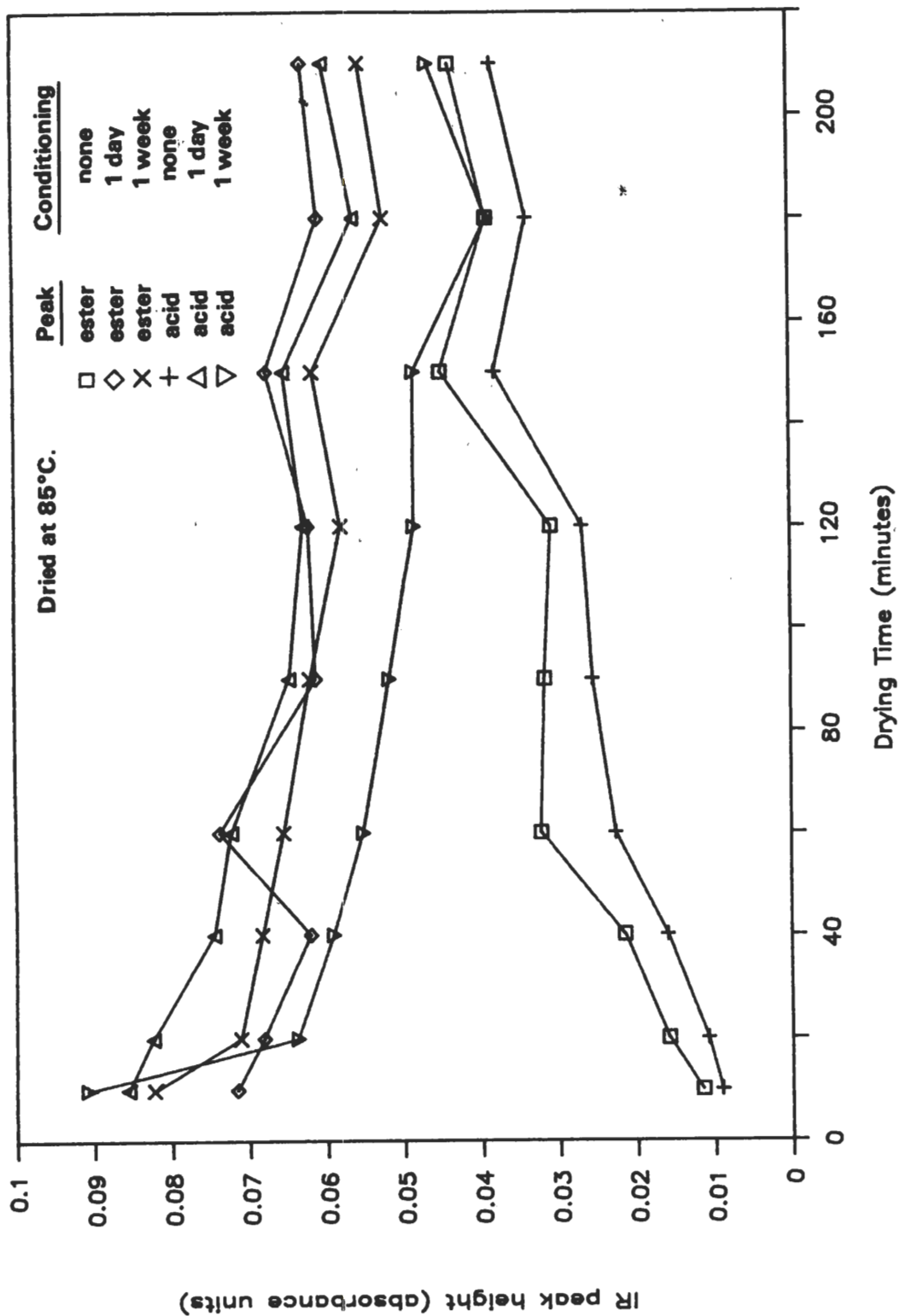


Figure 10. Development of the ester and acid IR peaks during conditioning.

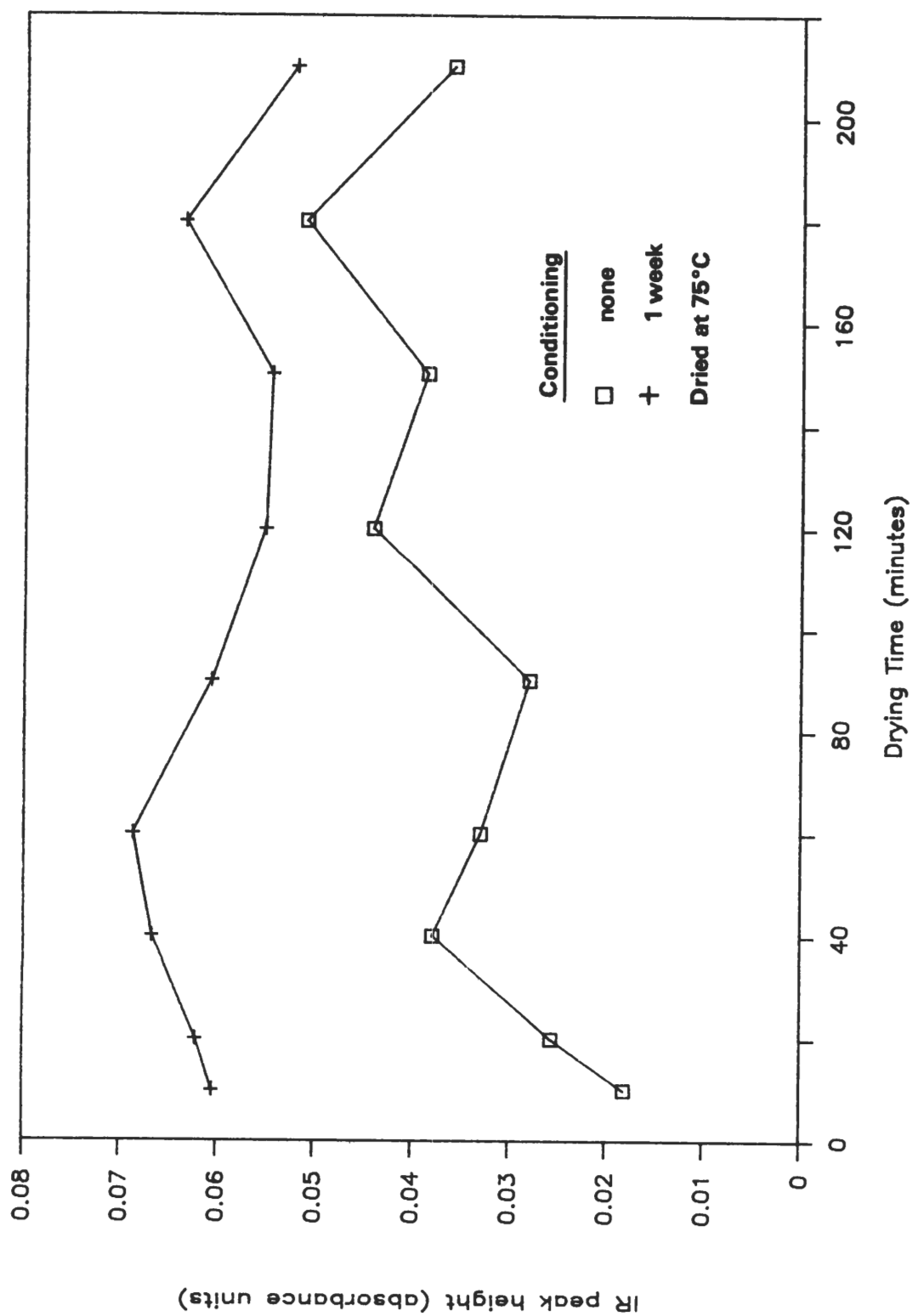


Figure 11. Development of the ester IR peak during conditioning. The sheet was extracted to remove the hydrolysis product after conditioning.