

A study of thermoxidative stability of natural and halocarbon waxes

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A number of contamination problems in the assembly of hybrid microcircuits have been traced to the presence in the systems of degraded waxes. No information was available on the composition or stability of the natural waxes which are used extensively in the etching, shipping and storing of hybrid microcircuit components. In this study, the composition and thermoxidative stability of three commercial waxes were defined. It was found that oxidation can occur at temperatures of 100° C; at high temperatures (150° C) the waxes are converted to insoluble chars. Vaseline, which is sometimes used as an additive, was found to have no effect on the stability of the waxes. Waxes made from poly(chlorotrifluoroethylene), available from Halocarbon Corporation, were found to be chemically stable and stable toward thermoxidation under the conditions used in the industry and are recommended as replacements for the natural waxes.

1. Introduction

Components for hybrid microcircuits are received by manufacturers embedded in various natural waxes. These waxes are used to secure silicone wafers to substrates during etching processes and for stability in orientation of the devices during shipment and storage. Vaseline (drugstore variety) is sometimes used as an additive to facilitate the handling of some components. In the manufacture of hybrid microcircuits, these waxes and vaselines are exposed to heat, air and etchants which brings about their degradation and results in bonding problems. In one of these steps, residual wax samples are exposed to temperatures as high as 400° C for short time periods. There was no information available from the suppliers on the composition of these waxes other than they were called "beeswaxes" and there was no data in the literature concerning the stability of these waxes toward heat and air.

The purpose of this study was three-fold:

- (1) to characterize these waxes both chemically and physically;
- (2) to determine the stability of these waxes toward heat and air and gain some insight into the mechanism of degradation; and

(3) to identify more stable waxes for this type of application.

2. Experimental details

2.1. Materials

Two of the natural waxes were obtained from Raytheon Corporation and Texas Instruments Co, suppliers of the components. The canning paraffin wax and vaseline used in this study were purchased locally. Halocarbon Products Corporation of Hackensack, NJ, provided the synthetic halocarbon waxes of three different melting points: no. 6-00, (m.p. 60 to 65° C) no. 8-00 (m.p. 75 to 80° C), and no. 12-00 (m.p. ~ 160° C).

2.2. Procedures

The waxes were aged under two different types of conditions;

- (1) for relatively long time periods and low temperatures, and
- (2) for short periods at high temperatures.

The intent of ageing for long time periods at lower temperatures was to obtain general information on the mode of degradation. The purpose of ageing for short time periods at high temperatures was to simulate one step in the pro-

cessing of hybridmicrocircuits. The specific conditions used are given below:

long term/low temperature: 100, 125, 150° C for 1 week in air circulating oven

short term/high temperature: 400° C for 35 to 45 sec.

The waxes were aged in the form of thin films (5 mg) on glass microscope slides. Volatility of the waxes at 400° C was determined by weight loss.

Both controlled and aged samples were characterized by the following techniques:

(a) melting point determination was done using a Fisher—Johns melting point apparatus, Model no. 2527A;

(b) the solubility of both controlled and aged samples was determined in tetrahydrofuran, ethyl alcohol, carbon tetrachloride, chloroform, and methylene chloride. Solubility experiments were done at ambient temperatures;

(c) infra-red spectra were taken on a Perkin—Elmer Model 21 double beam infra-red spectrophotometer. Soluble materials were cast from chloroform in a thin film on a salt (NaCl) plate. The insoluble aged materials were made into a potassium bromide pellet;

(d) gel permeation chromatography using a Waters Associates Liquid Chromatograph with differential ultra-violet detector and differential refractometer was employed to determine changes in distribution of molecular weights between the

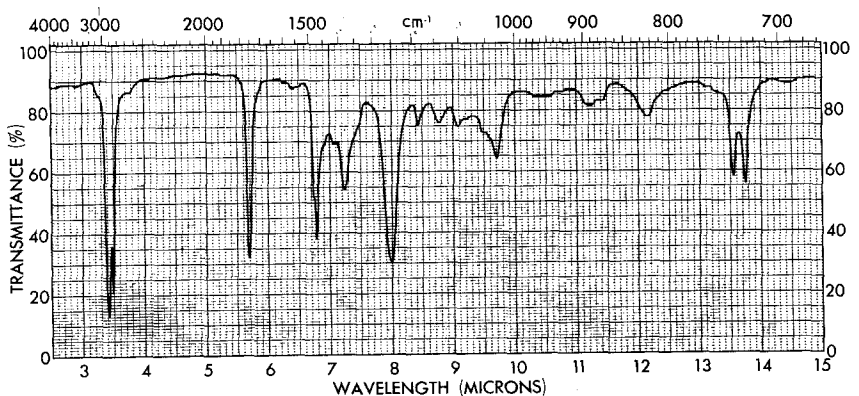
aged samples and the control samples. All samples were dissolved in tetrahydrofuran and passed through six columns packed with Styragel;

(e) softening temperatures were determined with a Perkin—Elmer thermomechanical analyser, Model TMS-1 that was equipped with a temperature control programme, Model UU-1. The temperature range used in these tests was from ambient to 120° C or the point at which the sample melted completely;

(f) concentrated nitric acid, concentrated hydrofluoric acid and concentrated sodium hydroxide were used to test the stability of the halocarbon waxes under etching conditions. Thin glass cover plates were coated with the waxes and placed in the concentrated solutions at 40 and 75° C for one week each, after which they were examined visually, and by infra-red spectroscopy for evidence of degradation.

3. Results and discussion

3.1. Characterization of the control waxes
Findley and Brown [1] reported that beeswaxes consist primarily of mixtures of olefinic and aliphatic esters. Infra-red spectra (Fig. 1) of our samples confirmed the presence of these compounds in the waxes supplied by Raytheon and Texas Instruments. Carbonyl and unsaturated bonds were also detected by strong ultra-violet absorbance. Several differences were noted between

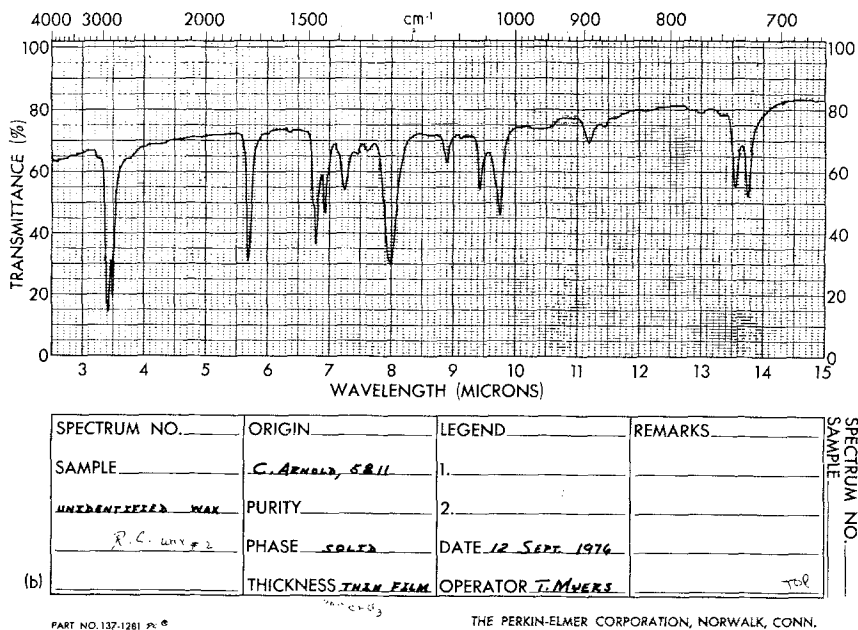


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS	SPECTRUM NO. SAMPLE
SAMPLE "IX BEEWAX" #1	C. ARNOLD, SB11	1.		
	PURITY	2.		
	PHASE SOLID	DATE 12 SEPT 1976		
(a)	THICKNESS THIN FILM	OPERATOR J. MYERS		

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Figure 1 Infra-red spectra of stock samples of (a) wax 1 and (b) wax 2.



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Figure 1 continued

wax 1 and wax 2, the two natural or beeswaxes:

(1) colour; wax 1 is yellow whereas wax 2 is white*,

(2) melting point; wax 2 melted 10 to 15°C higher than wax 1,

(3) oxygen content; wax 2 had a higher oxygen content than wax 1*, and

(4) wax 1 exhibited absorption bands in the infra-red at 690 and 820 cm⁻¹ which are characteristic of *cis* olefins and a *cis* olefin conjugated with a carbonyl group, respectively [2].

The plasticizer wax (wax 3) contained carbonyl groups (Fig. 2) and was composed of 6.52% oxygen. Paraffin has a general formula of C_nH_{2n+2} [3] and contains no oxygen or olefinic

bonds. Vaseline is, for the most part, a mixture of semi-solid hydrocarbons of the same general formula as paraffin [4].

Infra-red spectra (Fig. 3) of the halocarbon waxes confirmed that this wax was poly(chlorotrifluoroethylene). Thus, absorption peaks for carbon-hydrogen and carbonyl groups were absent; only absorption arising from C-F bonds (1100 to 1250 cm⁻¹) and C-Cl bonds (750 to 800 cm⁻¹) were observed.

3.2. Thermo-oxidative degradation studies

All organic materials are susceptible to oxidative degradation under appropriate conditions and to varying degrees depending upon the structure of

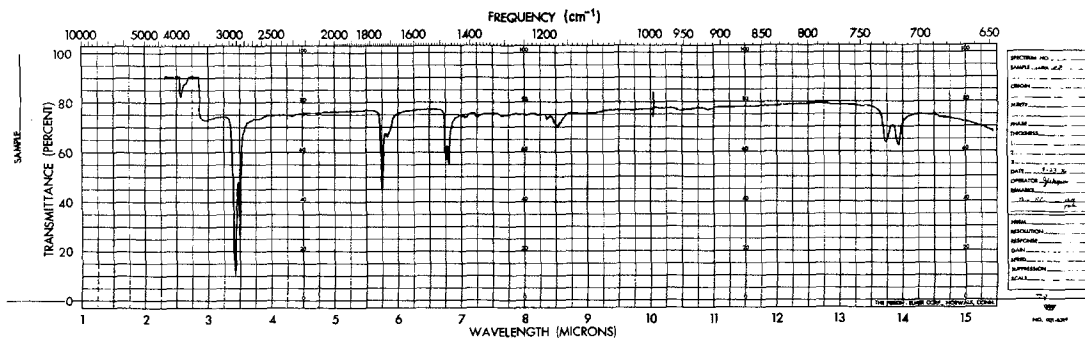


Figure 2 Infra-red spectrum of stock sample of plasticizer wax.

* White beeswax is usually made by bleaching yellow beeswax with chromic acid, hydrogen peroxide or ozone which probably accounts for the high oxygen content of wax 2.

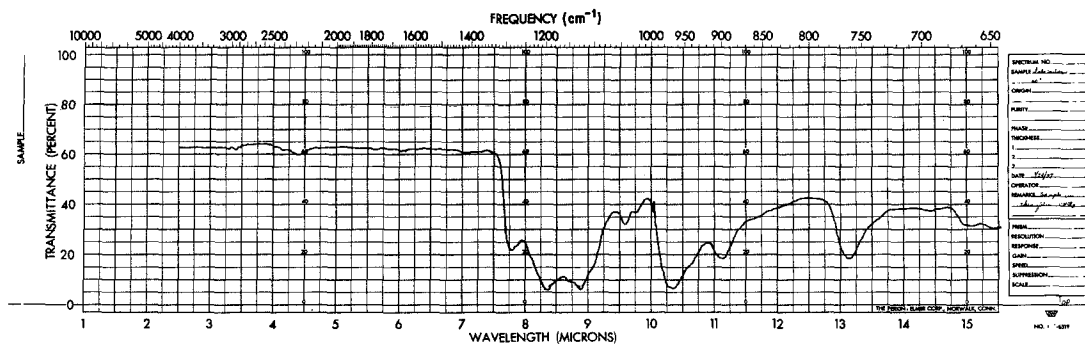
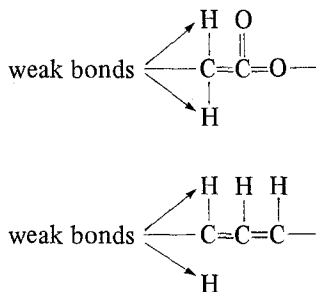
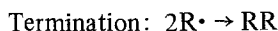
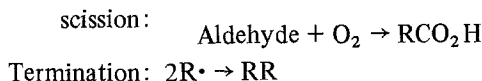
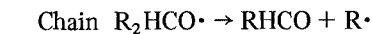
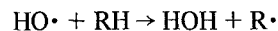
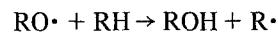
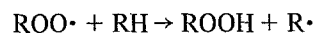
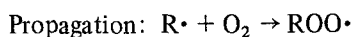
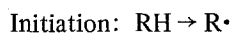


Figure 3 Infra-red spectrum of stock sample of halocarbon wax.

the molecule. Some oxidative reactions can lead to scission of molecular chains as well as cross-linking. Unsaturated compounds, branched compounds and those containing carbonyl groups are less stable toward autoxidation than saturated or straight chain materials [5]. The reduction in thermoxidative stability is attributable to the fact that the above structural features have the effect of weakening the strength of certain nearby C—H bonds. Thus, it has been reported that the bond dissociation energies of the C—H bonds α to a double bond (allylic) are $\sim 20 \text{ kcal mol}^{-1}$ less than those of vinylic bonds [6]. Similar activation of C—H bonds is observed when the hydrogen is α to carbonyl groups. Structures illustrating these effects are shown below.



It is generally accepted that autoxidation reactions of hydrocarbons are free radical chain reactions involving three basic steps: (1) initiation, (2) propagation, and (3) termination. Other reactions that can occur during oxidation are chain branching and chain scission. How these steps can occur with a long chain hydrocarbon molecule, RH, is illustrated below. At ordinary temperatures the rate of autoxidation is very slow, but at elevated temperatures such as those used in our ageing studies, autoxidation can be quite rapid.



In the case of beeswaxes, which, as mentioned above, consist primarily of saturated and unsaturated long chain esters, the chain reaction is probably initiated by rupture of the weak C—H bonds, α to double bonds, or carbonyl ester groups.

The thermoxidative instability of the natural waxes was demonstrated in our aged materials. The infra-red spectra of these waxes showed very little change after ageing at 100°C for one week, but the curves after 125°C ageing had variations in the carbonyl absorption (Fig. 4). Specifically, it was observed that the carbonyl absorption of unaged samples, which was assigned to the ester function, consisted of one single peak with a maximum absorption at 1740 cm^{-1} ; after ageing at 125°C , this peak broadened with "shoulders" appearing at 1730 and 1780 cm^{-1} , suggesting that other types of carbonyl groups are being formed (Fig. 4). After ageing at 150°C , broadening of the carbonyl absorption became more pronounced and was accompanied by an ingrowth of a

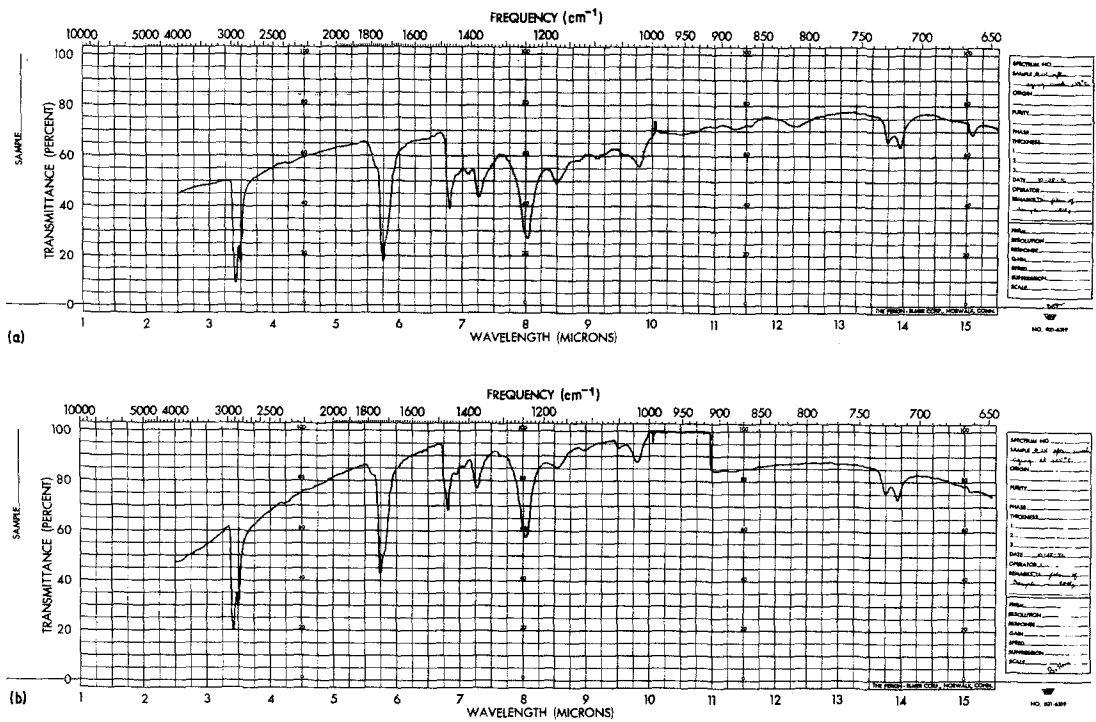


Figure 4 Infra-red spectra of (a) wax 1 and (b) wax 2, after ageing at 125° C for 1 week.

hydroxyl (OH) band at 3100 to 3500 cm^{-1} (Fig. 5). This finding suggests that cleavage of the ester group might have occurred to give carboxylic acid groups.

The idea that additional carbonyl groups are being introduced into the waxes as a result of thermoxidation is also generally supported by evidence based on elemental analysis. Thus, as shown in Table II, except for the white beeswax, quite significant increases in the oxygen content of the waxes was observed as a result of oven ageing. The presence of vaseline did not appear to impede the incorporation of oxygen into the

TABLE I Elemental analyses of natural waxes

	H (%)	C (%)	O (%)
Sample 1 (yellow beeswax)	9.40	68.98	21.72
Sample 2 (white beeswax)	8.90	62.68	28.43
Sample 3 (plasticizer wax)	12.64	80.85	6.52

waxes. At present, we can only speculate on the anomalous behaviour of the white beeswax, which actually showed a decrease in oxygen content. In this case, it is suspected that in the bleaching process, volatile oxygen-containing species were formed which vaporized during ageing and that this brought about the decreased oxygen

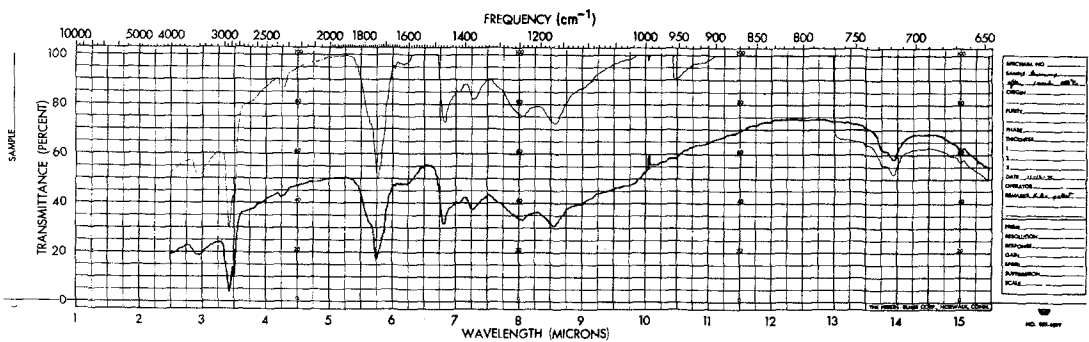


Figure 5 Infra-red spectrum of natural waxes after ageing at 150° C for 1 week.

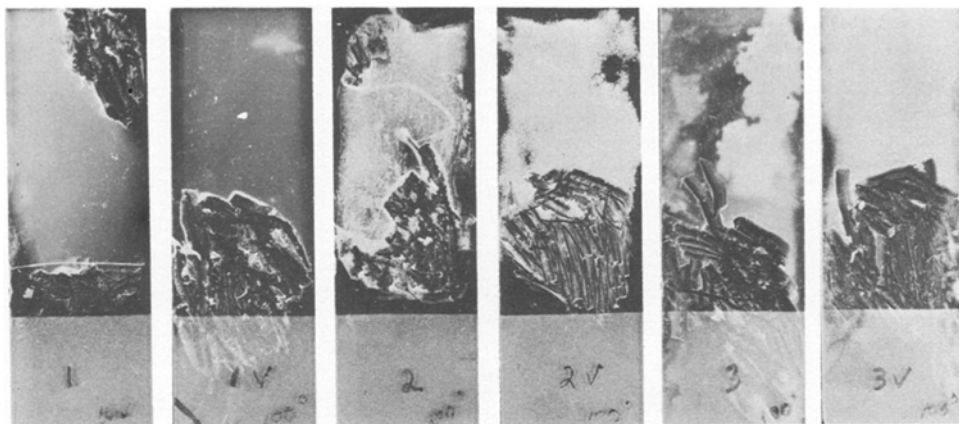


Figure 6 Natural waxes before ageing.

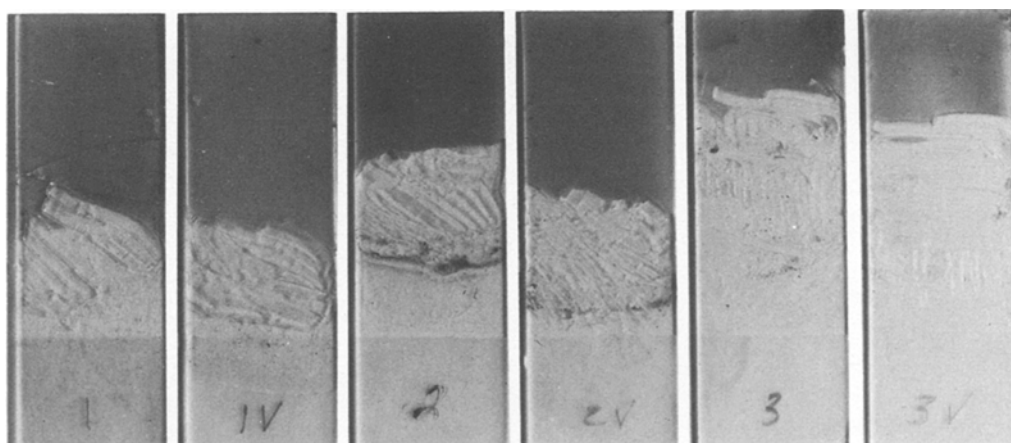


Figure 7 Natural waxes after ageing at 125° C for 1 week.

content. This pre-oxidation or bleaching step also apparently served to decrease the number of oxidation sites in the wax.

Melting and softening points of all the natural waxes decrease upon ageing at temperatures of 100 and 125° C. The melting points generally decreased 15 to 20° C and the softening points decreased 10 to 15° C. Solubility of the natural

waxes in common solvents increased after ageing at 100 and 125° C. The increase in solubility after ageing at these temperatures is tentatively attributed to two possible effects,

(1) oxidative chain scission which reduced the molecular weight of the waxes (this is supported by gel permeation chromatography data), and

(2) an annealing effect in which the extent of crystallinity of the waxes was reduced.

Figs. 6 and 7 show the observed visual differences in the natural waxes after ageing. Note the uniform darkening of the waxes at 125° C again supporting the thermoxidation at these temperatures.

The halocarbon waxes proved to be stable toward thermoxidation. The infra-red spectra did not change with the ageing procedure (Fig. 8). The peaks in the C—F and C—Cl stretching regions were present with no other group frequencies

TABLE II % oxygen in sample as function of temperature

	Control	100° C	125° C
1 (yellow beeswax)	21.72	21.84	25.06
1 with vaseline		18.86	25.60
2 (white beeswax)	28.43	27.72	22.33
2 with vaseline		23.60	21.10
Plasticizer wax	6.52	8.35	17.35
Plasticizer wax with vaseline		8.32	14.65

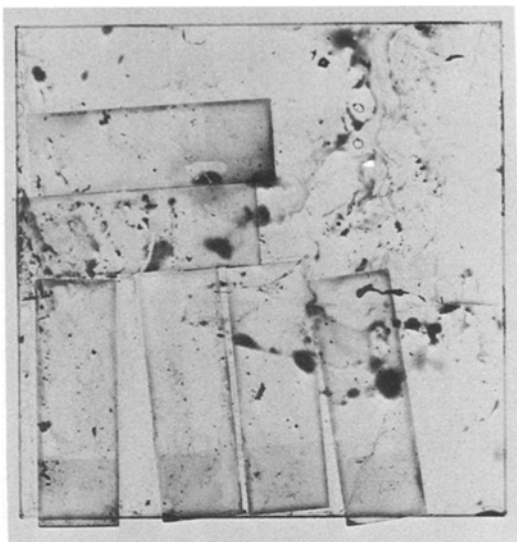


Figure 10 Natural waxes after ageing at 150° C for 1 week.

TABLE III % residue after 400° C heat treatment

Wax	Residue on glass cover plate after heat (%)
1	96.1
1V	93.98
2	94.30
2V	95.40
3	99.40
3V	96.60
6-00	0.00
8-00	0.30
12-00	7.50

lems alluded to in Section 1. In contrast, the halocarbon waxes either completely volatilized at 400° C or left only small residues.

That some chain scission occurred in the natural waxes at the lower temperatures is supported by gel permeation chromatography. There was a slight shift of peaks in the direction of lower molecular weights. The 150° aged materials were

insoluble in tetrahydrofuran so no GPC could be done.

None of the data we obtained indicated that vaseline interacted or catalysed or affected degradation. During the experiments with vaseline, it was observed that 60 to 70% of it evaporated at temperatures below the melting points of the natural waxes leaving only a small amount of higher molecular weight material to mix with the waxes. It should be noted that very small amounts of vaseline were used compared to the volume of the waxes.

Simulations of the etching process carried out on the halocarbon waxes resulted in no chemical attack on the waxes.

4. Conclusions and recommendations

In summary, the data substantiates that during the ageing and heating processes, cross-linking and oxidative degradation are taking place in the natural waxes. In contrast, the halocarbon waxes show greater chemical thermal stability. Thus, the natural waxes began to degrade at 100° C and decomposed extensively at temperatures > 125° C, whereas the halocarbon waxes did not start to decompose until temperatures of ~ 300° C were reached. Instead of volatilizing at processing temperatures, a large insoluble residue remained in the case of the natural waxes. The insoluble residue would certainly hinder bonding of the components to which it adheres. The halocarbon waxes volatilized with very little residue at 400° C. The small amount remaining is of a consistency which would probably break away from the bonding surface of the components when bonding pressure was applied.

The use of vaseline to facilitate removal of devices from glass plates is apparently not a factor in the changes taking place. At no time could we discover any effects due to the addition of vaseline to the waxes.

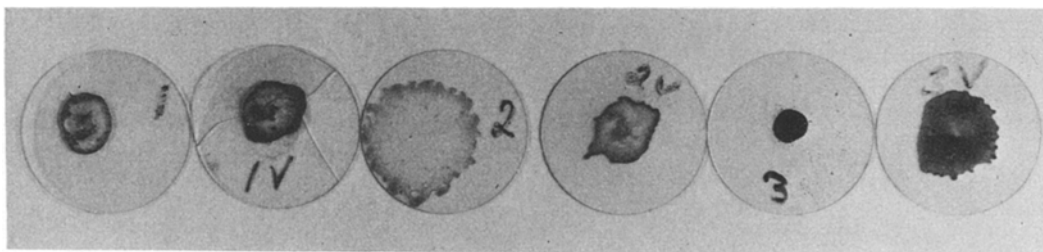


Figure 11 Residues of natural waxes after exposure to 400° C for 30 sec.

Recommendations are:

(1) if natural waxes are used, the temperatures involved in handling techniques should remain below 125° C;

(2) the use of high temperatures (~ 400° C) to volatilize the wax remaining on the devices does not have the desired effect, and the use of this technique is discouraged;

(3) on the basis of this study, it is recommended that halocarbon waxes be considered as possible replacements for natural waxes in the manufacture of electronic components and devices.

Acknowledgement

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