THERMAL DECOMPOSITION OF TOBACCO II. THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSES OF PIGMENTS FROM TOBACCO LEAF AND SMOKE CONDENSATE[1]

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INTRODUCTION

High molecular weight pigments have been isolated from both tobacco leaf and smoke condensate (12). These pigments have been shown to be complex and to contain moieties having molecular weights from <3,000 to >100,000 (5, 7, 13). Although the condensate pigment has been shown to resemble the leaf pigment certain differences in chemical and physical properties have been noted. In general, the condensate pigment appears to be less complex than the leaf pigment and contains a greater proportion of nonhydrolysable moiety (6, 7, 13).

Analyses of the pyrolytic products of the leaf pigment have releaved the presence of polynuclear aromatic hydrocarbons (4), bases (11) and phenols (10). As certain of these compounds exhibit biological activity, the contribution of the leaf pigment to the levels of these substances in smoke may be important. Reports have also appeared which indicate that certain high molecular weight brown polymeric substances in tobacco smoke exhibit cocarcinogenic activity when tested on laboratory animals (1, 9). These reports emphasize the need for further study of these high molecular weight substances in both tobacco leaf and smoke condensate.

The purpose of this investigation was to determine if differences exist in the thermal decomposition patterns of tobacco leaf and smoke condensate pigments which would aid in further establishing the properties of these pigments.

EXPERIMENTAL

Samples of pigment from flue-cured tobacco and from the smoke condensate of blended cigarettes were available for this work. The leaf pigment consisting of alcohol-soluble and alcohol-insoluble fractions was isolated by Chortyk et al. (4, 5). These fractions comprise 46 and 50%, respectively of the total pigment. The nondialyzable, weakly acidic smoke pigment was isolated from the smoke condensate of commercial cigarettes by Dymicky and Stedman (7). Since the leaf pigments from each of the four tobacco types are known to be similar in chemical and physical characteristics (5), the study was limited to a comparison of the pigments from flue-cured tobacco and the smoke condensate of commercial cigarettes.

The instrument used for the thermogravimetric analysis and the conditions employed were identical to those described earlier except that a heating rate of 6°C per minute was employed. The themogravimetric curves obtained were converted to their derivative curves (2). The differential thermal instrument used was an Aminco No. 4-4443 module which employed the temperature programmer of the basic thermogravimetric unit[3]. For differential thermal analysis the conditions employed were: air flow, 40 ml per minute; heating rate, 6°C per minute; amplification, 5; recorder sensitivity, 0.5 mv/in.

Prior to analysis, the pigments were dried for 16-24 hours *in vacuo* at 79°C. For thermogravimetric analysis, samples weighing 100 mg were run in Coors crucibles. For differential thermal analysis, 5 mg samples were run in stainless steel micro sample holders using alumina as the reference material. For each sample two or more runs were made and the results averaged.

RESULTS AND DISCUSSION

Although the pigments investigated in this study cannot be considered homogeneous, the results obtained do permit certain conclusions to be drawn regarding their complexity and thermal stability. For the alcohol-soluble (L_S) and alcohol-insoluble (L_I) fractions of leaf pigment the derivative curves obtained in both air and helium reveal differences over the entire temperature range **(Figures 1 and 2).** In air, the most noteworthy difference occurs between 500 and 600°C. At this temperature L_S loses weight at a rate almost three times that of L_I. This difference is also shown by the percentage weight losses in **Table 1.** In Zone V, 26.8% of L_S is lost compared with only an 8.0% loss for L_I. In helium, the most significant difference occurs between 700 and 800°C. Although no dw/dt maximum is seen for L_S, the curve for L_I reveals a pronounced maximum at 740°C. This difference is also reflected by the much higher percentage weight loss exhibited by L_I in Zone VI **(Table 1).** It therefor appears that unlike L_S, L_I consists of a component(s) which is thermally more stable under non-oxidative conditions.

A comparison of the weight losses for each of the leaf pigments in both air and helium reveals that in the inert atmosphere both fractions lose about the same total weight. In air, however, L_S loses about 20% more weight than L_I. From the percentage weight losses over the entire temperature range it is evident that the higher total weight loss exhibited by L_S is primarily due to the loss which occurs in Zone V. It therefore appears that the alcohol-soluble (L_S) leaf pigment contains a higher proportion of a more readily oxidizable component(s).

The derivative curves for the mixed leaf pigment (LP) and the smoke condensate pigment (SP) run in air are shown in **Figure 3.** For LP, three maxima are evident at 290, 450 and 570°C. In contrast, the derivative curve for SP reveals a more gradual increase in the rate of weight loss from ambient to about 400°C. At this point the rate of weight loss increases rapidly to a single pronounced maximum at 550°C. Therefore, unlike the

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[3]*Mention of a specific commercial product does not constitute endorsement by the U. S. Department of Agriculture or by the Kentucky Agricultural Experiment Station.*

Table 1. Percent weight loss for tobacco leaf and smoke condensate pigments

Zone °C	I 25-130	II 130-250	III 250-370	IV 370-500	V 500-650	VI 650-900	TOTAL
			AIR				
LEAF PIGMENT							
Alcohol Soluble	1.4	14.9	21.5	26.8	26.8	1.5	92.8
Alcohol Insoluble	1.5	8.0	27.5	27.0	8.0	0	72.0
Mixture[a]	1.5	10.0	25.8	26.8	16.0	0	80.1
Condensate Pigment	3.1	4.8	11.9	29.5	42.3	0	91.6
			HELIUM				
LEAF PIGMENT							
Alcohol Soluble	0.5	16.0	23.5	17.3	4.8	4.5	66.6
Alcohol Insoluble	1.5	7.5	20.0	12.0	4.5	20.0	65.5
Mixture[a]	1.3	8.7	23.3	14.0	5.5	12.5	65.3
Condensate Pigment	1.9	7.5	15.5	17.3	4.7	1.9	48.8

[a] Composed of 46% alcohol-soluble and 50% alcohol-insoluble leaf pigments on a weight basis

LP, a greater proportion of SP is more similar in thermal stability (Zone V). Data on the percentage weight losses in air are shown in **Table 1.** For LP, losses of 25.8, 26.8 and 16.0% occur in Zones III, IV and V, respectively. In these same zones SP loses 11.9, 29.5 and 42.3% of its total weight. Therefore, in contrast to the leaf pigment a greater percentage of the smoke pigment is lost at a higher temperature. The derivative curves for LP and SP in helium are shown in **Figure 4.** These are somewhat similar except that the curve for the LP reveals an additional dw/dt maximum in Zone VI. This accounts for 12.5% of the total weight loss and reflects the presence in LP of that portion of the alcohol-insoluble fraction which is quite stable. Apparently neither this component nor one of similar stability is present in SP. Total weight losses for LP and SP in both air and helium are also shown in **Table 1.** From these data it is apparent that compared with LP a larger percentage of SP is lost in air.

Comparison of the weight losses of both pigments in air and helium for the various temperature zones reveals that this greater SP weight loss is largely due to its greater weight loss which occurs in Zone V. It therefore appears that, in contrast to LP, a greater proportion of SP is lost as a result of oxidative degradation. However, as SP loses less of its total weight in helium, it appears that the smoke pigment is thermally more stable than the leaf pigment in the non-oxidative atmosphere. This is perhaps to be expected for two reasons: the smoke pigment, being a product of a burning cigarette, has previously been formed at and/or subjected to a temperature gradient as high as 884°C (14); and the atmosphere behind the cigarette coal, where a large proportion of smoke components are thought to originate, has been shown to be primarily one of reduction (8). Therefore, when subjected to conditions which are somewhat similar to those under which it was produced the smoke pigment would perhaps be more stable than the leaf pigment which had not been previously subjected to such conditions.

The differential thermal curves obtained for the leaf pigment fractions, the mixed leaf pigment and the smoke pigment are shown in **Figure 5.** In general, these curves complement the derivative curves and help to confirm the differences between these pigments. The curve for L_S shows exotherms around 510 and 580°C. For L_I two major exotherms occur at approximately 300 and 460°C. The curve for the mixed pigment appears to be a composite of each of its components with exotherms at approximately 300, 450, 500 and 560°C. For SP, a single major exotherm occurs at approximately 500°C. The number of major exotherms and the temperatures at which they occur agree quite well with the thermogravimetric data and help to substantiate these data **(Figures 1-4).**

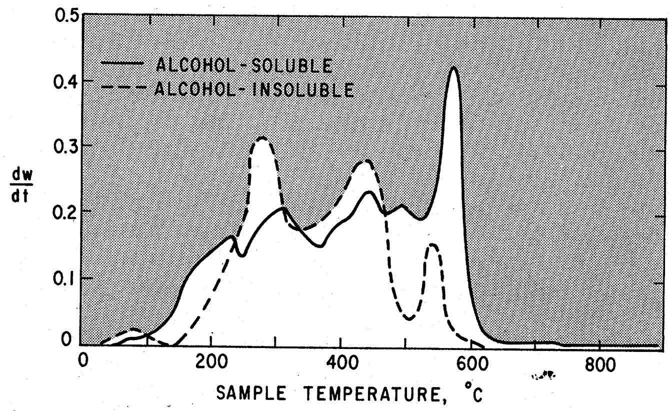

Figure 1—Derivative thermograms of alcohol-soluble and alcohol-insoluble leaf pigments in air.

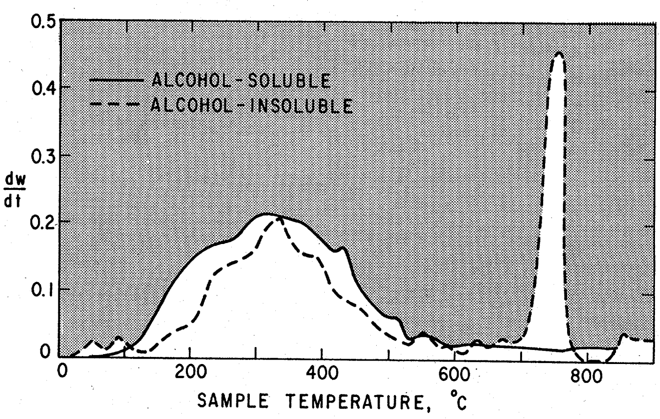

Figure 2—Derivative thermograms of alcohol-soluble and alcohol-insoluble leaf pigments in helium.

In general, the results obtained from DTA and TGA support previous findings which show that pigments from tobacco leaf and smoke differ in composition and molecular weight (3, 5, 13). In a previous publication the presence of high molecular weight pigment in cigarette smoke was postulated as possibly having been caused by the eruption of the tobacco cells and the expulsion of cellular contents into the smoke stream as a result of the sharp thermal gradient behind the cigarette coal (13). The results of this present study indicate that if this occurs the resulting pigment undergoes significant alteration during the process.

SUMMARY

Thermogravimetric and differential thermal analyses were employed to characterize the thermal decomposition of pigments from tobacco leaf and smoke condensate. Alcohol-soluble and alcohol-insoluble fractions of leaf

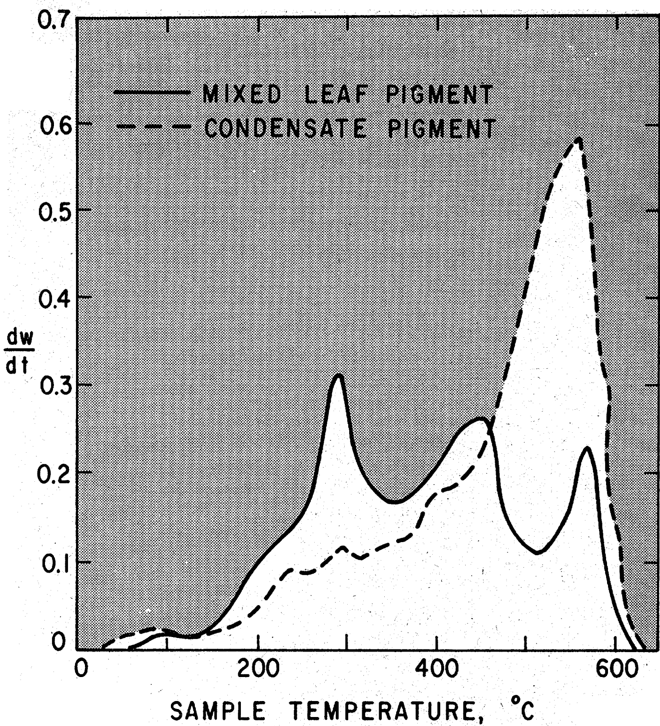

Figure 3—Derivative thermograms of mixed leaf pigment and condensate pigment in air.

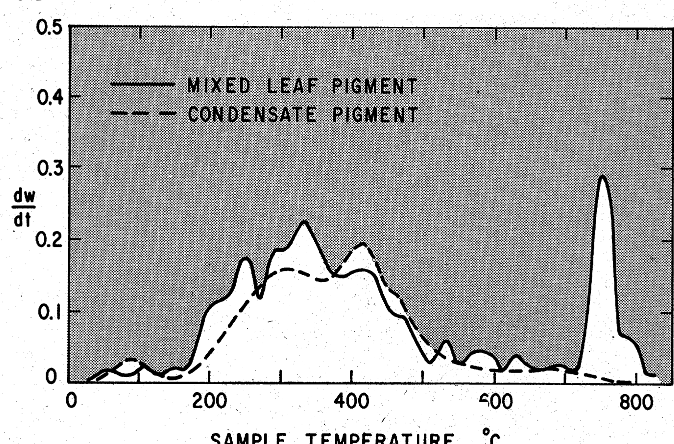

Figure 4—Derivative thermograms of mixed leaf pigment and condensate pigment in helium.

pigment from flue-cured tobacco, a mixture of these pigments and smoke pigment from commercial cigarettes were investigated. In general, the data obtained in air and helium reveal definite differences among these pigments. The alcohol-soluble fraction loses a higher percentage of its weight at a higher temperature and contains a higher proportion of a more readily oxidizable component than the alcohol-insoluble fraction. In this respect, the alcohol-soluble fraction of the leaf pigment is more similar to the smoke pigment. The data obtained for the smoke pigment indicate that it is less complex and undergoes oxidative degradation to a greater extent than the leaf pigment. However, in helium it is thermally more stable than the leaf pigment. The differential thermal curves obtained for each of these pigmetns complement the thermogravimetric data and help to substantiate these differences. These findings substantiate previous work on significant differences in structure and thermal stability of pigments from leaf and smoke condensate.

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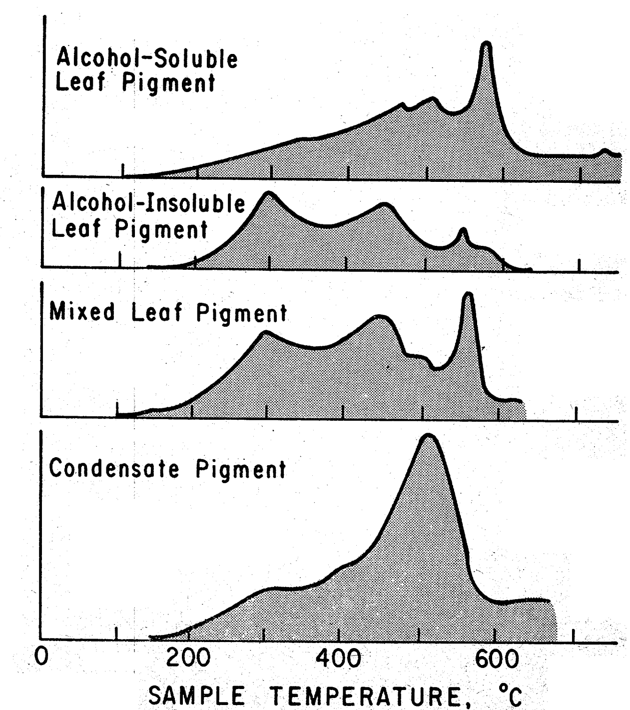

Figur 5—Differential thermograms of leaf pigment fractions, mixed leaf pigment and condensate pigment. Ordinate expressed as Δ T.