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COMPOSITIONAL ANALYSIS OF WATERBORNE PAINT SYSTEMS BY THERMOGRAVIMETRY

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ABSTRACT

Thermogravimetry is shown to be a rapid method for fingerprinting waterborne paint composites, and with sensitive instrumentation this technique permits identification of paint types with samples as small as 1 mg. Examination of a series of acrylic and PVA-based composites, containing varying levels of binder, kaolin, $CaCO_3$ and TiO_2, show that the technique may also be used for quantitative determination of these major components. Generally, binder and $CaCO_3$ content can be determined with reasonably high precision, which in favourable cases approaches ±0.5%. The determination of kaolin and TiO_2 (by difference) are subject to much larger errors, particularly at low kaolin concentrations. Assay of PVA-based composites is complicated by an apparent interaction between acetic acid liberated from the resin and the $CaCO_3$ filler. This interference leads to inflated values for binder content with concomitant reduction in $CaCO_3$ level.

INTRODUCTION

Recently we have been faced with the problem of identification of dry paint films, frequently handicapped by small sample sizes. Whereas the overall binder type may be ascertained by IR examination [1] and information as to the nature and content of fillers and pigments may be derived from AA analysis for elements such as Ca or Ti, the methods are time-consuming and the results sometimes equivocal. The ideal method is one which gives an overall *fingerprint* of the whole paint formulation which can then be matched with standard compositions. The method should be: rapid, applicable to small samples (1–20 mg), capable of unambiguous interpretation and it should preferably provide quantitation of components.

It occurred to us that thermogravimetry (TG) might be an appropriate candidate for this task since such techniques have been extensively applied to the analysis of polymer composites as exemplified by the determination of oils, carbon black and inorganic fillers in rubber compounds and vulcanisates. An added incentive for investigating this technique has been the great improvements brought about in commercial instrumentation by the

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TABLE 1

Composition of standard wet paint samples

Component	136A	136B	136C	136D	136E	136F	136G	136H	136I	136J	136K
Water	32.79	33.29	26.31	26.66	31.17	29.55	27.93	31.63	29.98	28.32	26.46
$CaCO_3$	41.22	41.22	2.00	2.00	31.42	21.61	11.81	31.42	21.61	11.81	2.00
TiO_2 (A)	6.00	6.00	20.00	20.00	9.50	13.00	16.50	9.50	13.00	16.50	–
TiO_2 (B)	–	–	–	–	–	–	–	–	–	–	20.00
Kaolin	–	–	16.00	16.00	4.00	8.00	12.00	4.00	8.00	12.00	15.69
Acrylate resin	7.91	–	15.91	–	9.91	11.91	13.91	–	–	–	–
PVA resin	–	8.33	–	17.12	–	–	–	10.53	12.73	14.92	17.43
Additives	12.08	11.16	19.78	18.22	14.00	15.93	17.85	12.92	14.68	16.45	18.42
Total	100	100	100	100	100	100	100	100	100	100	100
Solids	(55.7%)	(56.1%)	(54.5%)	(55.7%)	(55.4%)	(55.1%)	(54.8%)	(56.0%)	(55.9%)	(55.8%)	(55.7%)

introduction of data processing and computerised control which have greatly enhanced their viability for routine analysis.

Consequently, we have examined in some detail the application of TG to the analysis of dry paint films derived from waterborne paints. The results of this study are now reported.

EXPERIMENTAL

Wet paints of known but variable composition (Table 1) were dried as thin films on glass plates initially in a forced air draft and subsequently overnight in an oven at 50 °C.

The whole paint films, as well as individual paint components, were examined over the temperature range 30–1000 °C using a Mettler TA3000 thermogravimetric analyser. Sample sizes were generally 10–30 mg for paint films and 1–15 mg for pure components, such as the binder or extenders. All samples were contained in the supplied alumina crucibles equipped with lids. Depending on the nature of the sample, either inert (nitrogen) or interactive flow gases (oxygen or carbon dioxide) were used, as indicated in the text. Dynamic experiments were carried out at a heating rate of 40 °C $\min^{-1}$. Both lower (20 °C $\min^{-1}$) and higher (100 °C $\min^{-1}$) rates were briefly examined. The lower rate produced results very close to the 40 °C $\min^{-1}$ heating rate, whereas the highest rate proved to be slightly inferior for quantitative work.

Numerous dynamic, step-programmed and isothermal procedures were evaluated and it was found that the most appropriate method depended on the nature of the overall paint composite as well as the aim of measurement, e.g. *fingerprint* identification or quantitative determination of components. However, the most generally useful techniques are summarised below:

Method 1: dynamic run 30–1000 °C under nitrogen.
Method 2: dynamic run 30–1000 °C under oxygen.
Method 3: isothermal at 375 °C under oxygen for 20 min followed by cooling to 30 °C and dynamic run 30–1000 °C under oxygen or nitrogen.

Weight loss steps were computed by the TC10 data processor which forms an integral part of the Mettler system. Manual checking of the computed results showed excellent agreement.

Calibration of the temperature scale was accomplished by the Curie point method employing the standard materials supplied with the instrument.

RESULTS AND DISCUSSION

The components of waterborne (emulsion) paints readily amenable to study by TG are those present in amounts exceeding about 1% w/w and

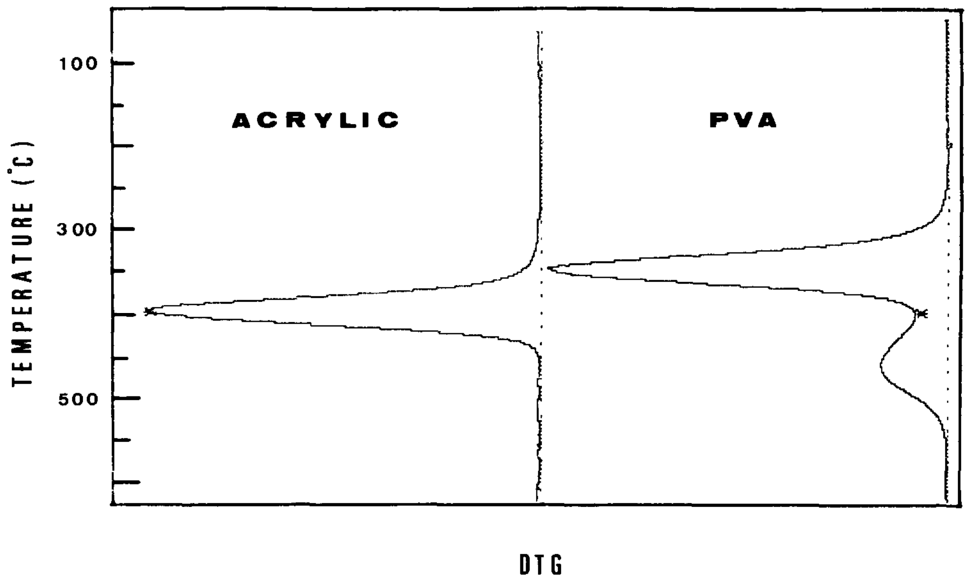
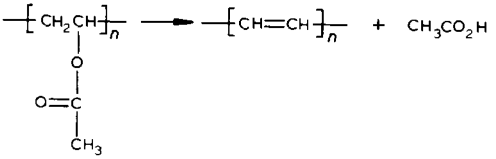


Fig. 1. Derivative weight loss curves for acrylic and PVA binders under nitrogen.

comprise: solvent, binders, extenders and pigments. A preliminary screening was enacted to determine the thermal profiles of the pure components and to establish whether the components exhibited characteristic and reproducible weight loss steps in the temperature range from ambient to 1000°C.

Decomposition of paint binders

PVA, PVA copolymers and acrylic copolymer resins form some of the major classes of paint binder for waterborne resins. As anticipated from the known degradation behaviour of these polymers [2] the PVA and acrylic polymers show distinct and characteristic weight loss curves under nitrogen (Fig. 1). Both PVA and its copolymers show an initial weight loss (under nitrogen) in the temperature range 340–350°C due to side-chain elimination of acetic acid:

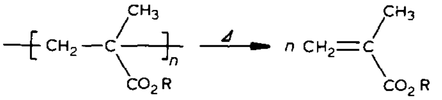


$$\left[\mathrm{CH_2CH}(\mathrm{O{-}C({=}O){-}CH_3})\right]_n \longrightarrow \left[\mathrm{CH{=}CH}\right]_n + \mathrm{CH_3CO_2H} \qquad (1)$$

The observed weight loss of 71 ± 1% w/w for pure PVA compares favourably with the calculated value (69.8% w/w). A copolymer of PVA with ethylhexylacrylate (15% w/w) showed a weight loss proportional to the PVA content.

At higher temperatures fragmentation of the polymeric residue occurs with loss of volatile products (~ 22% w/w) and the formation of a carbonaceous residue (~ 6–7% w/w) under nitrogen. Use of an oxidising atmosphere, however, leads to a quantitative burn-off of the polymer after an initial loss of acetic acid.

Acrylic polymers, notably copolymers of MMA with higher acrylates, show a simple, single-step degradation profile with effectively quantitative weight loss under nitrogen. The decomposition corresponds to the usual chain unzipping of the polymer (2) which is known to occur almost quantitatively for alkylmethacrylates.



$$-\!\left[CH_2-\underset{CO_2R}{\overset{CH_3}{C}}\right]_n\!- \xrightarrow{\Delta} n\,CH_2=\underset{CO_2R}{\overset{CH_3}{C}} \qquad (2)$$

It follows from the above analysis that thermogravimetry should be effective in both distinguishing different binder types as well as in quantitative determination.

Weight loss characteristics of extenders

Kaolin

Kaolin or China Clay is a hydrated silicate of aluminium of approximate empirical formula, $Al_2O_3 \cdot 2(SiO_2) \cdot 2H_2O$, and is widely used as an extender in paint formulations. On heating under nitrogen or oxygen at 40°C min^{-1} the water loss occurs as a single step with a DTG maximum in the range 530–560°C for samples in the range 1.6–12 mg. The temperature for maximum rate of weight loss appears to increase slightly with sample size. The overall weight loss for kaolin samples heated to 1000°C at 40 K min^{-1} and cooled to room temperature was found to be $13.1 \pm 0.1\%$ w/w for samples analysed in triplicate. This value is somewhat less than that of 13.95% w/w calculated on the basis of the above formula.

Assessment of the weight loss profile of kaolin from a dynamic run reveals that the breadth of the weight loss envelope increases with sample size. This is illustrated in Fig. 2 which relates the percentage weight loss within the temperature range 450–650°C to sample size. It can be seen that the weight loss within these temperature limits decreases from about 11 to 10% w/w as the sample size is increased from 1.6 to 13 mg. This observation is important for precise determination of kaolin content from dynamic measurements.

Calcium carbonate

Calcium carbonate is present as an extender (or, low-cost white pigment) in varying amounts in most waterborne paint systems. At 40°C min^{-1}

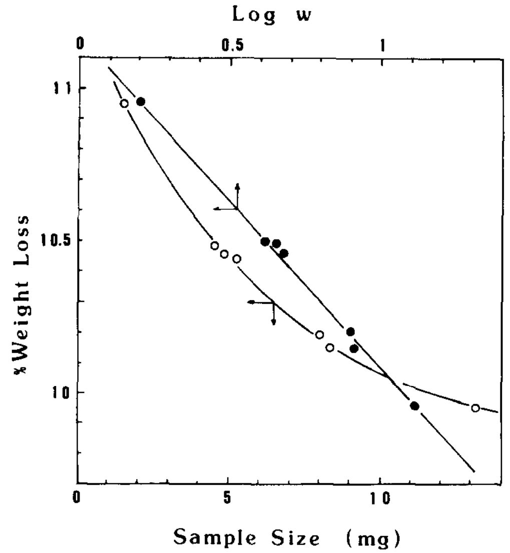


Fig. 2. Dependence of kaolin weight loss on sample size within the temperature range 450–650 °C.

under nitrogen or oxygen, thermal decomposition of the carbonate to calcium oxide occurs with DTG maxima in the range 733–902 °C depending on sample size.

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (3)$$

The marked dependence of the decomposition temperature on sample size is a direct consequence of the equilibrium nature of the decomposition reaction — the extent of decomposition at a particular temperature being dependent on the partial pressure of carbon dioxide, which in turn is related to sample size. This is clearly demonstrated by dynamic runs under an atmosphere of carbon dioxide where the peak decomposition temperature is > 910 °C even for small samples. A linear relationship between log(sample size) and temperature is found to hold for samples in the range 0.5–23 mg.

Weight loss of calcium carbonate in dynamic runs determined over the temperature range 600–1000 °C was generally very close to the theoretical value of 44.0% w/w as calculated on the basis of the empirical formula.

Thermal behaviour of titanium dioxide

Titanium dioxide is widely used as a white pigment in premium quality waterborne paints. Two grades of titanium dioxide designated A and B were examined. Over the full temperature range and under oxygen, the two grades showed an average weight loss of 2.1 and 3.3% w/w, respectively, after cooling to room temperature. The sample characterised by the highest weight loss was known to be surface-treated with an organic material. No distinct weight loss steps were discernible, although for both samples 90% of the loss occurred below 500°C.

Thermal analysis of paint composites

A series of test paint samples based on both PVA and acrylic resins and containing varying levels of binder, extenders and pigments (Table 1) was subjected to TG analysis. Typical thermal curves (Fig. 3) show that there are no substantial synergistic effects since the peak decomposition temperatures in the composite material are closely similar to the pure components. Thus, qualitatively the thermal curves may indeed be used as a *fingerprint* of the composite since the binder type and the presence or absence of kaolin and calcium carbonate may readily be discerned.

Quantitative analysis of the paint composite is, however, a more rigorous application and is complicated, at least in the PVA systems, by overlap of the secondary resin decomposition with that of kaolin. This problem may, however, be overcome by selective burn-off of the binder using an isothermal step analysis method as discussed below.

Determination of binder content

Acrylic binders may generally be determined from a dynamic run under nitrogen whereupon the weight loss occurring in the temperature range 250–450°C is a measure of the binder content. Small weight losses occur in

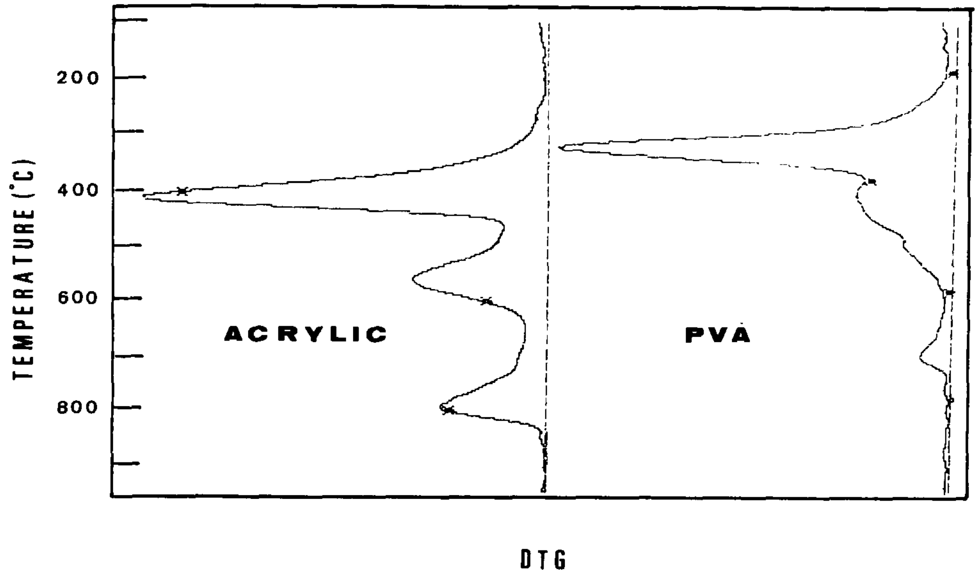


Fig. 3. Derivative weight loss curves for acrylic and PVA paint composites under nitrogen.

TABLE 2

Comparison of calculated and determined binder content for acrylic based paints

Sample No.	Binder content (% w/w)		Volatiles [b] (% w/w)
	Calculated	Determined [a]	
136A	14.2	14.8, 14.3	
136E	17.9	18.3, 17.4	1.5, 1.6
136F	21.6	21.7	2.1
136G	25.4	25.6	2.5
136C	29.2	29.1, 28.9	

[a] Using Method 1, weight loss calculated for range 250–450°C.

[b] Weight loss over temperature range 30–250°C.

the temperature range from ambient to 250°C and these are thought to be due mainly to components such as residual monomer, solvents and possibly surfactant and other volatile additives. The extent of weight loss in this region is approximately 9% of the binder weight (Table 2).

Comparison of the determined binder content with that calculated for the prepared composition shows quite good correlation over a fairly wide range of paint compositions (Table 2).

PVA paint composites were assayed under oxygen to effect quantitative decomposition/combustion of the binder. Two distinct procedures were used, viz. a dynamic scan and an isothermal weight loss treatment at 375°C. Comparison of the weight loss characteristics with the known binder content is summarised in Table 3. Generally the agreement is much less satisfactory than for the analysis of acrylic binders described above. For the dynamic run the weight loss was calculated over two temperature ranges 200–450 and 250–450°C, the upper limit being chosen to avoid interference by kaolin. The wider temperature range measurement tends to overestimate the binder

TABLE 3

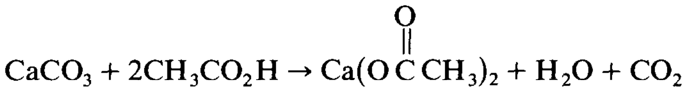
Comparison of calculated and determined binder content for PVA based paint composites

Sample	Calculated binder content (% w/w)	Weight loss (% w/w)			Volatiles [a] as % binder	$CaCO_3$ (% w/w)
		Dynamic		Isothermal		
		200–450°C	250–450°C	375°C		
136B	14.9	16.0	14.5	17.8	20	72
136H	18.8	20	17.8	21.9	17	56
136I	22.7	24.3	22.9	26.5	17	39
136J	26.7	28.4	27.1	30.5	14	21
136D	30.7	30.6	28.1	32.6	6	3.6
136K	31.3	31.4	30.4	33.9	8	3.6

[a] Calculated from the expression: [(isothermal wt. loss% − % binder content)/(% binder content)] × 100.

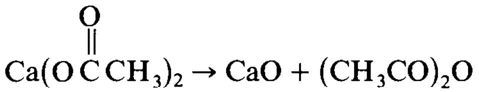
content except with high binder samples. The restricted temperature range shows the reverse effect.

The isothermal values, as expected, give too high an estimate of the PVA content as these figures include other components which are volatile below 250°C. In contrast to the acrylic resins the weight loss due to volatiles does not appear to be proportional to the binder content and varies from as high as 20% of binder content to as little as 6–8%, compared to an almost constant 8–9% for the acrylic resins. Interestingly this variation parallels the $CaCO_3$ content of the composite (Table 3). This suggests the possibility of an interaction between the degrading PVA and the filler. A possible candidate might be reactions such as:



$$CaCO_3 + 2CH_3CO_2H \rightarrow Ca(O\overset{\overset{O}{\|}}{C}CH_3)_2 + H_2O + CO_2$$

and



$$Ca(O\overset{\overset{O}{\|}}{C}CH_3)_2 \rightarrow CaO + (CH_3CO)_2O$$

where the overall effect is for the liberated acetic acid to catalyse displacement of carbon dioxide from the calcium carbonate. Such a reaction would be consistent with the observed characteristics of the anomalous behaviour, viz:

(i) dependent on $CaCO_3$ content;
(ii) not observed with acrylic resins; and
(iii) leading to increased weight loss values.

This side reaction complicates the analysis and is probably the chief reason for the poorer reproducibility of the analytical results in the case of PVA paint composites.

Determination of kaolin content

Precise determination of the kaolin content of the paint composite is hindered by relatively small weight change accompanying the dehydration of the kaolin as well as the tendency for the weight loss to overlap with binder degradation. In order to minimise the overlap with either residual binder decomposition or incipient $CaCO_3$ decomposition the weight loss in a restricted temperature range (475–625°C) was used for estimation of the kaolin content. Appropriate corrections were made for dependence of weight loss on sample size (Fig. 2) as discussed above. (Over this temperature range the weight loss decreased from about 10% w/w for a 1.4 mg sample to 9% w/w for a 17 mg sample.)

Two distinct TG procedures were used. The initial single-step approach involved a dynamic heating run under nitrogen (acrylic samples) or oxygen

TABLE 4

Comparison of calculated and determined kaolin contents in acrylic and PVA based paint composites

Sample	Kaolin content (% w/w)		
	Calculated	Determined	
		Single step [a]	Two step [b]
Acrylic			
136E	7.22	13.7	8.0
136F	14.5	–	13.9, 14.6
136G	21.9	23.2	–
136C	29.4	32.7	–
PVA			
136H	7.1	–	6.9
136I	14.3	14.9	13.9
136J	21.5	19.1	20.3
136K	28.2	–	42.4, 37.7 [c]
136D	28.7	–	28.9

[a] Data from dynamic run under nitrogen (acrylic) or oxygen (PVA).

[b] Data from Method 3 involving isothermal pretreatment with oxygen at 375°C for 20 min.

[c] As for b except 35 min at 375°C.

(PVA samples). The drawback of this method is that the binder decomposition tends to slightly overlap the kaolin dehydration. This problem is reduced by a two-step procedure where the binder is burnt off isothermally at 375°C under oxygen, followed by a separate dynamic run to determine the kaolin. The results of these procedures are summarised in Table 4.

It is clear that the single-step procedure tends to overestimate the kaolin content and this must largely be attributed to overlap with weight loss steps of other components. The overlap errors are greatly compounded by the necessity of using a scaling factor of between ×10–11 for calculation of the kaolin content. On the other hand the two-step procedure gives much better agreement with an average deviation from the actual content of less than 4%. The only exception is sample 136K where the determined kaolin content is excessively high even after a prolonged burn-off (30 min at 375°C). The problem may be associated with the high binder content of this sample and the use of a coated TiO_2 pigment.

Determination of $CaCO_3$

Generally, for these samples, the calcium carbonate content is taken to be proportional to the weight loss occurring over the temperature range 650–1000°C. As pointed out earlier the actual temperature of maximum rate of weight loss is somewhat variable being dependent on the carbonate content of the sample. However, a distinct and resolvable weight loss step is

TABLE 5

Comparison of calculated and determined $CaCO_3$ contents in acrylic and PVA based paint composites

Sample	Calcium carbonate content (% w/w)		
	Calculated	Determined	
		Under N_2	Under O_2
Acrylic			
136C	3.7	5.5, 5.3, 4.4	
136G	21.6	21.7, 22.1	
136F	39.2	40.3, 40.3	38.0, 38.1
136E	56.7	56.5	54.9
136A	74.0	74.6, 74.3	
PVA			
136D	3.6		4.2, 4.2, 3.6
136K	3.6		3.4, 3.6, 3.6
136J	21.2		19.3, 19.4, 18.7
136I	38.6		35.9, 36.9
136H	56.1		53.4, 54.8
136B	73.5		72.3, 70.9, 69.8

normally discernible. The results of the analysis for both PVA and acrylic based composites are summarised in Table 5.

Overall, reasonable agreement is observed between the calculated and determined values. Not surprisingly, samples containing low carbonate contents are susceptible to the greatest error and this is probably aggravated by a tendency for the weight loss steps of these samples to overlap with the kaolin decomposition. It is noticeable that the analyses of PVA composites show a tendency towards lower $CaCO_3$ contents than their acrylic counterparts. This may be related to interactions between the PVA binder and carbonate discussed above. On the other hand, the difference may be related to the use of an oxygen atmosphere since acrylic resins give slightly lower carbonate values under an oxidising atmosphere. The cause of this behaviour is not clear. Conceivably the acrylic carbonate values may be inflated by the degradation of organic residues in the carbonate region, or, an oxidising atmosphere may promote the formation of acidic degradation products which interact with the carbonate as speculated above in the case of PVA.

Determination of TiO_2

Thermogravimetry does not permit the direct determination of TiO_2 as this material is effectively inert over the temperature range 30–1000°C. However, determination of the residual ash content together with a knowledge of the kaolin and $CaCO_3$ content of the composite do permit the

TABLE 6

Comparison of calculated and determined TiO_2 content of the paint composites

Sample	Residue (% w/w)		TiO_2 content (% w/w)	
	Calculated	Determined	Known	Determined
Acrylic				
136A	51.98	51.67	10.8	10.2
136E	54.80	55.02	17.2	16.8
136F	57.66	57.41	23.6	22.9
136G	60.59	60.21	30.1	28.4
136C	63.52	62.61	36.7	32.0
PVA				
136B	51.62	51.55	10.7	12.0
136H	54.22	54.06	17.0	18.1
136I	56.85	56.32	23.3	24.4
136K	61.20	60.09	35.9	26.2
136J	59.43	58.74	29.5	31.1
136D	62.12	60.94	35.9	34.3

estimation of TiO_2 or similar inert material. Thus the content of TiO_2 type A may be related to the residue by the formula:

$$\text{Residue (\% w/w)} = 0.979 \times \%\ TiO_2\ \text{(Type A)} + 0.560 \times \%\ CaCO_3 + 0.869 \times \%\ \text{kaolin}$$

where the various scaling factors, viz. 0.979, 0.560, 0.869 are the weight fraction of the respective materials at room temperature after heating to 1000 °C.

Comparison of the predicted and determined values are summarised in Table 6. It can be seen that the determined ash content corresponds closely to that predicted from the above relationship using the values of TiO_2, $CaCO_3$ and kaolin content as prepared. This clearly demonstrates that the binder and other minor additives are quantitatively removed on heating to 1000 °C and that the scaling factors are approximately correct.

However, determined values of TiO_2 derived from the above relationship and making use of the experimental values of kaolin and $CaCO_3$ show considerable scatter from the known value at least for certain samples. This arises since the errors in the TiO_2 content are compounded by errors in the assay of $CaCO_3$ and kaolin as well as in the ash content. In general the closest agreement is found for acrylic samples of high $CaCO_3$ content where the above errors are minimised.

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