

**DETERMINATION OF RESIN CONTENT  
OF GLASS FIBER-POLYESTER LAMINATES  
CONTAINING A CALCIUM CARBONATE FILLER**

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# *Contrails*

## FOREWORD

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## ABSTRACT

The presence of calcium carbonate filler in unoriented glass-fiber reinforced polyester laminates introduces appreciable errors when determining the resin content by the accepted method.

The temperature range, 538° to 593°C, required to burn off the resin is higher than that at which calcium carbonate begins to dissociate. The reduction of calcium carbonate to calcium oxide and the subsequent evolution of carbon dioxide results in a greater loss in weight than would be expected if no filler were present. A quantitative method of restoring the carbon dioxide to the reduced filler consists of treating the residue with an excess of a concentrated ammonium carbonate solution to convert the calcium oxide formed back to calcium carbonate.

Specimens were prepared from predetermined amounts of resin, glass-fiber mat and calcium carbonate to give the following composition, by weight: resin, 50 percent; glass fiber, 37.5 percent; and calcium carbonate, 12.5 percent.

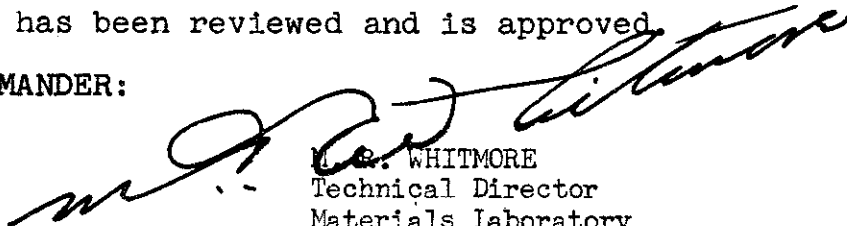
The specimens were ignited to constant weight in a muffle furnace, cooled, and weighed. The residue was treated with ammonium carbonate and the increase in weight due to absorbed carbon dioxide was determined. Hot 3N hydrochloric acid was added to the treated residue in an attempt to remove, quantitatively, the calcium carbonate.

Results obtained in these experiments indicate that treatment of the residue with ammonium carbonate will reduce the error in the resin content from an average 3.75 percent to less than 0.1 percent. The acid treatment cannot be used to give quantitative determination of the calcium carbonate, the resin or the glass since about 10 percent of the glass dissolves in this treatment.

## PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. G. WHITMORE  
Technical Director  
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## SUMMARY

A reasonably accurate determination of the resin content of glass fiber-polyester laminates containing calcium carbonate filler may be made by following the normal procedure for finding the resin content and then correcting the values obtained upon ignition by converting any reduced calcium oxide back to the carbonate by treating the ignited residue with ammonium carbonate.

A quantitative measurement of calcium carbonate cannot be made with treatment of the ignited residue with hydrochloric acid because certain constituents of the glass are dissolved by the acid.

## INTRODUCTION

Inert fillers are often used in the production of unoriented glass-fiber reinforced polyester laminates. The most widely used inert filler for this application is precipitated calcium carbonate. Previous work has indicated that the presence of this specific filler introduces appreciable errors in the results obtained by the presently accepted method of determining resin content (1)<sup>a/</sup>. Since the quantitative measurement of the components of glass-reinforced plastic laminates is often necessary to determine whether the required specification limits are being met, a modification of the method of test was developed to correct for errors introduced by the calcium carbonate filler. This report describes a reasonably accurate, rapid method for determining the resin content of laminates containing a polyester resin, unoriented glass mat and calcium carbonate filler.

## GENERAL CONSIDERATIONS

The resin content of a glass fiber-polyester laminate which does not contain a filler is normally obtained by igniting a specimen to weight equilibrium in a muffle furnace at 538 to 593°C and measuring the loss in weight of the specimen. This loss of weight on ignition is then corrected for the loss in weight caused by volatilization or decomposition of the fiber finish to give the resin content (1).

When specimens containing calcium carbonate filler are used, the loss of weight on ignition in the muffle furnace is considerably greater than that of the original amount of resin present. Part of this excess loss arises from the volatile part of the fiber finish while the remainder is carbon dioxide evolved from the filler. This appears reasonable since at temperatures above 525°C calcium carbonate begins to dissociate into calcium oxide and carbon

<sup>a/</sup> Numbers in parenthesis refer to references given at the end of this report.

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dioxide (2). The amount of dissociation of calcium carbonate is dependent upon the temperature and the partial pressure of the carbon dioxide in the furnace atmosphere and may also be effected by the pyrolysis of the organic matter present in the resin and fiber finish. The dissociation of calcium carbonate into calcium oxide and carbon dioxide is a three-phase, two-component equilibrium system. Application of the phase rule,  $P + V = C + 2$ , indicates one degree of freedom, that is, either temperature or pressure, if arbitrarily fixed, will define the state of equilibrium. Since the normal partial pressure of carbon dioxide in the atmosphere is 0.24 mm, the carbon dioxide contained in the system will be evolved when its partial pressure exceeds that of the carbon dioxide in the atmosphere. This pressure is initially reached at a temperature of approximately 525°C. Consequently, when the temperature is raised above this point, as is required in the method for resin content determination, the carbon dioxide is evolved into the space immediately above the solid constituents, calcium carbonate and calcium oxide. If fresh air is allowed to pass over the specimen, as in a ventilated muffle furnace, some of the carbon dioxide will be drawn out of the crucible and the system of calcium carbonate, calcium oxide and carbon dioxide will no longer be in equilibrium. More carbon dioxide must be evolved from the calcium carbonate to regain the partial pressure necessary for an equilibrium state. A continuous flow of air, then, will result in a continuous evolution of carbon dioxide. The amount of carbon dioxide lost during the period of ignition is dependent not only upon the temperature used but also upon the length of time required to burn the resin.

Two methods were considered for treating the residual matter left after ignition to obtain a corrected resin content. These were the removal of the calcium carbonate and calcium oxide by solution in a dilute acid and the reconversion of the calcium oxide to calcium carbonate by replacing the carbon dioxide lost on ignition. The former method involving the use of hot 3N hydrochloric acid to dissolve the calcium carbonate and calcium oxide could not be used for two reasons. First, to be certain of the amount of carbon dioxide lost on ignition the specimen would have to be ignited to weight equilibrium at temperatures above 1000°C to completely convert the calcium carbonate to calcium oxide. These high temperatures would produce errors in the weight of volatile materials by causing fusion of the glass

fibers and the resultant entrapment of unburned carbon particles from the resinous materials present. Secondly, it was found that the acid dissolves certain constituents in the glass fibers. This results in a loss in weight greater than that of the original weight of calcium carbonate and eliminates the possibility of a quantitative measure of the filler present in the laminate.

To regain the weight lost through dissociation of the calcium carbonate, the ignited residue may be treated in some manner to convert the calcium oxide back to calcium carbonate without the formation of other constituents. This conversion may be obtained quantitatively by treating the oxide with an excess of concentrated ammonium carbonate solution. The excess unreacted ammonium carbonate, which dissociates into ammonia, carbon dioxide and water at 58°C (3), is then removed by evaporating the solution to dryness.

An increase in residual weight obtained with the ammonium carbonate treatment represents quantitatively the amount of carbon dioxide lost on ignition. Subtracting this increase in weight of the ignited residue and the loss in weight arising from the destruction of the fiber finish from the original loss in weight should give a correct value for the original resin content of the plastic laminate.

## PREPARATION OF SPECIMENS

Specimens of known composition were prepared using the following materials:

- Resin: Selectron 5003, an unsaturated polyester resin manufactured by the Pittsburgh Plate Glass Company.
- Glass Fiber: Unoriented glass mat, 2 oz/sq ft, manufactured by the Bigelow Glass Fiber Division of the Bigelow-Sanford Carpet Company.
- Filler: Precipitated calcium carbonate, assay 99.96 percent, manufactured by the Merck Company.



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Catalyst: Luperco ATC, 50 percent benzoyl peroxide and 50 percent tricresyl phosphate, manufactured by the Lucidol Division of the Novadel-Agene Corporation.

The composition of the specimens is given in table 1, and duplicates the general range found in some commercial items. The specimens were prepared by adding a predetermined amount of each component to a weighed porcelain crucible to give a total weight of about 3 grams. This weight is approximately that of a glass fiber-polyester laminate specimen 1 by 1 by 1/8 inch. Quantities of components used were as follows: resin, 50.0 percent; glass mat (as received) 37.5 percent; and filler, 12.5 percent (25.0 percent based on weight of resin used).

The glass fiber used in this work was obtained from a single piece of mat measuring two feet square. The eighteen fiber finish content specimens measured approximately 1 by 5 inches while the specimens used in the resin content determination measured approximately 1 by 4 inches for group 1 and 1 by 3 inches for groups 2 and 3. The average value of 1.5 percent based on the total weight of glass mat as received, was taken to apply to all of the specimens in the three test groups.

## PROCEDURES

The glass mat and calcium carbonate filler were dried at 110°C for one hour to eliminate any traces of moisture, and cooled to 23°C in a desiccator charged with calcium chloride. The resin was catalyzed with Luperco ATC, 2 percent by weight of resin. The components were separately weighed into a porcelain crucible on an analytical balance. After curing the resin at 110°C for 25 minutes and cooling to room temperature, the specimen was placed in a muffle furnace at 538 to 593°C and ignited to constant weight which required about 1.5 hours. Higher temperatures were avoided to prevent fusion of the glass and the resultant entrapment of unburned carbon particles. Upon removal from the furnace, the specimen was cooled to room temperature in a desiccator and reweighed on an analytical balance. The weight loss on ignition is equal to the weight of the

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resin, the volatilized or decomposed part of the fiber finish, and any carbon dioxide evolved from the dissociation of the calcium carbonate filler.

The residual material remaining in the crucible was reacted with an excess of a concentrated solution of ammonium carbonate. The specimen was evaporated to dryness at 80°C to drive off the excess ammonium salt, then heated at 110°C to constant weight. The specimen was again weighed after cooling in a desiccator to room temperature. The increase in weight obtained from treatment with ammonium carbonate is the weight of the carbon dioxide absorbed by the ignited filler and is equal to the carbon dioxide evolved from the filler during ignition in the furnace.

The resin content in weight percent is:

$$R = \frac{[W_1 - W_2 - W_3 - (W_4 - W_3)]}{W_1} \times 100$$

$$\text{or } R = \frac{W_1 - W_2 - W_4}{W_1} \times 100$$

where  $W_1$  = original weight of specimen  
 $W_2$  = weight of fiber finish  
 $W_3$  = weight after ignition, and  
 $W_4$  = weight after ammonium carbonate treatment.

Following the weighing after the ammonium carbonate treatment, each specimen was transferred from the crucible to a beaker and enough 3N hydrochloric acid was added to completely cover the glass fiber. After heating the acid for five to ten minutes, or until solvent action ceased, the glass residue was filtered off and repeatedly washed with boiling distilled water until a silver nitrate test of the filtrate was negative for chlorides.

The filter paper containing the acid-insoluble glass fiber residue was placed in a crucible and the filter paper burned off. The specimens were allowed to cool to room temperature in a desiccator prior to the final weighing. Two methods were used to determine the amount of acid soluble glass. In method A, the soluble constituents were calculated from the difference in weight between the original corrected glass fiber content and the acid-insoluble residue. Values for method B were calculated from the difference in weight between the total acid-soluble constituents and the original filler content.

## RESULTS

The test results obtained with the ammonium carbonate treatment are given in table 2. Of three groups of specimens tested, group 1 contained resin and glass, and groups 2 and 3, resin, glass and calcium carbonate filler. All of the specimens were treated according to the procedures previously outlined except for the omission of the ammonium carbonate treatment for group 3.

The control specimens in group 1 had a measured resin content of about 0.01 percent less than the original resin content after correcting the loss on ignition for the fiber finish content. Subsequent treatment with ammonium carbonate gave a measured resin content of about 0.06 percent less than the original resin content based on the original specimen weight. This indicates that a slight error may be introduced by the retention of a small amount of unvolatilized ammonium carbonate or its products, either adhering to or reacting with the glass fiber or some of its constituents. The difference in these values results from an average weight increase of about 2 milligrams after the ammonium carbonate treatment. After the ammonium carbonate treatment the difference between the measured resin content and original resin content for the specimens in group 2 was about 0.01 percent based on the original weight of resin. The specimens in group 3 were not treated with ammonium carbonate. The measured loss on ignition, after correcting for the fiber finish content, was about 3.75 percent more than the original resin content based on the original specimen weight. This error is attributed to the loss in weight of the calcium carbonate filler due to evolution of carbon dioxide.

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The three groups of specimens were treated with hot 3N hydrochloric acid to determine the acid-soluble portion of the glass fiber-calcium carbonate residue. The values obtained for the acid-soluble constituents of the glass fiber, given in table 3 under method A, ranged from 5.82 to 21.97 percent and averaged 10.38 percent for all eighteen specimens, based on the weight of glass fiber, less the volatile fiber finish content.

The volatile part of the finish on the glass fiber was obtained according to the method used for determination of resin content (1). The loss in weight resulting from ignition in a muffle furnace under the usual conditions is assumed to be the volatile part of the fiber finish and is reported as weight percent of the original glass fiber. Results obtained on the 2 oz mat in this and previous work have indicated a wide variability of the amount of finish not only from roll to roll but also from location to location within a roll. The results given in table 4 indicate that the variation obtained is high.

The variation in fiber finish may introduce an error in the measured resin content the magnitude of which is dependent upon the uniformity of the fiber finish and the proportions of glass and resin used in the laminate.

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Table 1. Composition of Specimens for Resin Content Determination.

Specimen	Original Composition, Weight Percent <sup>a</sup>				
	Resin <sup>b</sup>	Calcium Carbonate Filler	Glass Fiber, as Received	Volatile Fiber Finish <sup>c</sup>	Glass Fiber <sup>d</sup>
Group I					
1	49.96	none	50.04	0.75	49.28
2	50.02	none	49.98	0.75	49.23
3	49.95	none	50.05	0.75	49.30
4	50.10	none	49.90	0.75	49.15
5	50.02	none	49.98	0.75	49.23
6	49.96	none	50.04	0.75	49.29
Group II					
7	50.37	12.45	37.18	0.56	36.62
8	49.97	12.58	37.45	0.56	36.89
9	49.86	12.48	37.66	0.56	37.10
10	50.00	12.49	37.51	0.56	36.95
11	50.03	12.50	37.47	0.56	36.91
12	50.19	12.50	37.31	0.56	36.74
Group III					
13	50.06	12.52	37.42	0.56	36.86
14	50.04	12.54	37.42	0.56	36.86
15	50.13	12.43	37.44	0.56	36.88
16	50.14	12.50	37.36	0.56	36.80
17	49.88	12.63	37.49	0.56	36.93
18	50.22	12.46	37.32	0.56	36.76

- a. Original specimen weights ranged from 2.9974 to 3.0293 grams.
- b. Previously catalyzed with Luperco ATC, 2 percent by weight.
- c. Based on 1.5 percent of the original weight of glass fiber.
- d. Glass fiber, as received, less volatile fiber finish.

Table 2. Resin Content Determination<sup>a</sup>.

Specimen	Loss of Weight on Ignition	Fiber Finish	Corrected Ignition Weight Loss <sup>b</sup>	Carbon Dioxide Absorbed <sup>c</sup>	Measured Resin Content	Original Resin Content	Difference in Resin Content, Measured Less Original
	wt %	wt %	wt %	wt %	wt %	wt %	wt %
<b>Group I</b>							
1	50.68	0.75	49.93	0.07	49.86	49.96	-0.10
2	50.84	0.75	50.09	0.06	50.03	50.02	0.01
3	50.61	0.75	49.86	0.07	49.79	49.95	-0.16
4	50.87	0.75	50.12	0.04	50.08	50.00	-0.02
5	50.97	0.75	50.22	0.12	50.10	50.02	0.08
6	50.61	0.75	49.86	0.04	49.82	49.96	-0.14
Average	50.76	0.75	50.01	0.07	49.95	50.00	-0.06
<b>Group II</b>							
7	52.72	0.56	52.16	1.79	50.37	50.37	0.00
8	53.17	0.56	52.61	2.73	49.88	49.97	-0.09
9	55.64	0.56	55.08	5.11	49.97	49.86	0.11
10	55.38	0.56	54.82	4.78	50.04	50.00	0.04
11	51.82	0.56	51.26	1.28	49.98	50.03	-0.05
12	55.52	0.56	54.96	4.73	50.23	50.19	0.04
Average	54.04	0.56	53.48	3.40	50.08	50.07	0.01
<b>Group III</b>							
13	53.96	0.56	53.40	-	53.40	50.06	3.33
14	56.02	0.56	55.46	-	55.46	50.04	5.43
15	53.55	0.56	52.99	-	52.99	50.13	2.86
16	55.32	0.56	54.76	-	54.76	50.14	4.61
17	52.05	0.56	51.49	-	51.49	49.88	1.61
18	55.42	0.56	54.86	-	54.86	50.22	4.64
Average	54.39	0.56	53.83	-	53.83	50.08	3.75

- a. All values are based on original weight of the specimen.
- b. Loss of weight on ignition less fiber finish. Results obtained by normal method of determining resin content.
- c. Increase in residual weight after treatment with ammonium carbonate.
- d. Corrected ignition weight loss less amount of carbon dioxide absorbed.



Table 3. Determination of Acid-Soluble Constituents of Glass in Glass Fiber-Polyester Plastics.

Specimen	METHOD A <sup>a</sup>				METHOD B <sup>b</sup>			
	Glass Fiber Content <sup>c</sup> wt %	Acid-Insoluble Glass wt %	Acid-Soluble Glass wt %	Acid-Soluble Glass wt %f	Acid-Soluble Glass and Filler wt %	Filler <sup>d</sup> Content wt %	Acid-Soluble Glass wt %	Acid-Soluble Glass wt %f
<b>Group I</b>								
1	49.28	45.11	4.18	8.47	4.28	none	4.28	8.69
2	49.23	45.61	3.62	7.35	3.61	none	3.61	7.33
3	49.30	46.43	2.87	5.82	3.03	none	3.03	6.14
4	49.15	43.85	5.30	10.78	5.32	none	5.32	10.83
5	49.23	44.05	5.18	10.51	5.10	none	5.10	10.37
6	49.29	44.97	4.32	8.76	4.46	none	4.46	9.04
Average	49.25	45.00	4.25	8.62	4.30	none	4.30	8.73
<b>Group II</b>								
7	36.62	34.13	2.49	6.79	14.93	12.45	2.48	6.79
8	36.89	33.84	3.05	8.28	15.72	12.58	3.14	8.52
9	37.10	34.57	2.53	6.82	14.91	12.48	2.43	6.55
10	36.95	32.52	4.43	11.98	16.88	12.49	4.39	11.87
11	36.91	34.50	2.40	6.50	14.96	12.50	2.46	6.64
12	36.74	33.26	3.48	9.47	15.94	12.50	3.44	9.36
Average	36.87	33.80	3.06	8.31	15.56	12.50	3.06	8.29
<b>Group III</b>								
13	36.86	30.50	6.36	17.25	15.54	12.52	3.02	8.21
14	36.86	29.80	7.06	19.16	14.18	12.54	1.64	4.44
15	36.88	34.48	2.40	6.51	11.96	12.43	-0.47	-1.27
16	36.80	28.71	8.09	21.97	15.97	12.50	3.47	9.44
17	36.93	33.03	3.90	10.56	14.92	12.63	2.30	6.22
18	36.76	33.30	3.46	9.42	11.28	12.46	-1.18	-3.20
Average	36.85	31.64	5.21	14.15	13.98	12.51	1.46	3.97



Table 3. Determination of Acid-Soluble Constituents of Glass in Glass Fiber-Polyester Plastics. (Cont'd)

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- a. Acid-soluble glass calculated from original corrected glass fiber content less residue insoluble in hydrochloric acid.
- b. Acid-soluble glass calculated from loss of weight on treatment with hydrochloric acid less original filler content.
- c. Original glass content less volatile fiber finish.
- d. Original calcium carbonate content.
- e. Based on original weight of specimen.
- f. Based on weight of glass.

Table 4. Volatile Glass-Fiber Finish Content.

<u>Area Sampled</u>	<u>Number of Specimens</u>	<u>Volatile Fiber Finish Content</u>		
		<u>Average<sup>a</sup></u>	<u>Standard Deviation</u>	<u>Range</u>
		<u>wt %</u>	<u>wt %</u>	<u>wt %</u>
1 sq ft	8 <sup>b</sup>	2.06	0.11	1.92-2.23
4 sq ft	18 <sup>b</sup>	1.51	0.11	1.28-1.66
125 yd roll	20 <sup>b</sup>	1.34	0.25	0.79-1.94
125 yd roll	20	1.52	0.36	0.93-2.26

- a. Average loss in weight after ignition in muffle furnace.
- b. These specimens were obtained from the same 125-yard roll of glass mat.