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PROPERTIES OF CARBON FIBERS WITH VARIOUS COATINGS

Volker Seegel and Paul McMahon

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16. Abstract

It is shown that all high-modulus carbon fibers are durable with respect to thermal oxidation in air. Among the more widely used and economical materials with low modulus, Celion displays particularly good oxidative durability at high temperatures. This, in contrast to other materials, is due to the low content of sodium and potassium in Celion-carbon fibers. It is also noted that improved characteristics are attained in Celion carbon fiber/polymide systems when fibers are used with high temperature-resistant polymide coatings.

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1. INTRODUCTION /1*

The first extensive investigations concerning the properties of carbon fibers in high-quality epoxy resin-based composites at temperatures up to 450° K were made at the beginning of the seventies [1]. In the following years polyimide resins were developed which made possible the production of void-free composite materials of a highly reproducible quality [2]. Since these resins can be used for composite materials with working temperatures from 533 - 644° K, it is necessary that the reinforcing fibers for such high-quality composite materials exhibit especially good oxidative resistance. Loss of weight in air was selected as the criterion for determining the best available carbon fibers [3]. Some of the values determined are presented here according to most recent revised status.

PAN-based fibers were preferred since all commercially available carbon fibers with high strength and a modulus of 200 - 240 GN/m^2 are derived from this precursor.

2. OXIDATIVE RESISTANCE OF THE FIBER

Commercially available carbon fibers with a modulus between 200 and 500 GN/m^2 are prepared from a number of different presursors by using a great variety of processes. These fibers exhibited exceptionally great differences in weight losses after thermal aging in air with various combinations of time and temperature. The conditions selected simulate either real conditions with respect to time and temperature or extreme conditions (increased temperatures), in order to accelerate the aging process, here the loss of weight. Both the real conditions and the accelerated conditions will be described in this paper.

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* Numbers in margin indicate pagination of original foreign text.

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Accelerated aging:

It was found that the heating of carbon fibers for 24 hours at 648° K in air allows the division of commercially available fibers into three classes. The data obtained from a large number of carbon fibers are shown in Table I. From this table it can be seen that three classes of oxidative stability were .

There are a few very stable fibers which lose less than /2
1% of their weight under these conditions. This group includes the fibers GY-70 and Celion G-50. Both fibers have a very high carbon content of > 99% and during fabrication are subjected to temperatures up to 2,300° K. A second group of fibers of medium stability can be seen from the table, whose weight loss is between 1 - 5%. The third group of obviously very unstable fibers shows weight losses up to 10%. All fibers of the third group have a carbon content of 91 - 95% and have in common, that they are subjected during the fabrication process to only the relatively low temperature of about 1500° K. The Celion fiber, which exhibits a similarly low carbon content and which was produced at a similar temperature as the fibers of the third group, exhibits a different behavior and has an unusually high thermal stability, which places it into the middle second group. It must be noted that values were determined for all three high-strength Celion fibers and that they are shown in this table because of the similarity of the values; in the following all three high-strength Celion fibers will be treated as one product.

It can also be observed that Celion G 50 exhibits a thermal stability better by an order of magnitude than other carbon fibers with a similar modulus. Thus Celion G 50 is found in the group of the most stable types of carbon fibers, while other fibers with comparable modulus fall into the group of medium stability.

Aging under real conditions:

The maximum temperature stressability of polyimide composite materials is between 530 and 650° K. Thus an average temperature of 588° K was selected for measuring the thermal stability as a function of time. A test temperature of 588° K seems to be more realistic than the maximum stressability at 650° K, since for most of the applications to be expected the maximum temperature stressability will be used only briefly, while a stressing of 588° K can be expected absolutely over a long period of time. The results of carbon fibers with promising stability are shown in Table II, whereby one of the most widely used fibers Thornel 300 was chosen as a comparison.

It becomes clear that Celium 3,000, 6,000, and 12,000 exhibit /3 a considerably better thermal stability than the selected comparison product and that it approaches the HTS-fiber with respect to resistance to oxidation in air. Celion G 50 was also investigated and exhibits excellent stability. The HTS-fiber was used for a comparison since it represents a fiber with stability comparable to that of the Celion fibers, but the production of this PAN-based material with higher modulus is more costly. Finally the values of the Celion fibers were determined with samples having a standard finish (facing) as well as with unfaced samples and it can be seen, that the loss in weight caused by the finish takes place at the beginning of the heat treatment. After this a faced and an unfaced material acts the same way.

The values of the Celion types 3000, 6000, 12,000 and that of the higher-module type G 50 are shown in figure 1. The difference in the thermal stability can be clearly seen by the shape of the curve which represents the relative degree of the oxidative decomposition.

Since many applications for carbon fiber composites are subjected to working temperatures of only about 533° K, it was of interest to determine the loss of weight as a function of time at this temperature. The corresponding results are shown in Table III. A smaller number of fibers were tested, only for the purpose of determining differences in orders of magnitude. It is shown that Celion as well as HTS are exceptionally stable under these conditions, while T 300 suffers an additional significant loss in weight. Again the early loss in weight, caused by oxidation and vaporization of particles from the facing of the Celion fiber, can be seen while the further increase of the weight loss remains insignificant.

3. CARBON CONTENT AND TRACES OF METAL

Techniques for chemical analysis of the fiber composite materials:

The carbon content of most of the carbon fibers tested here was determined by a modified Pregl method. The metal analysis was conducted with a combined ash/emission-spectrograph technique. Surfur and chlorine were determined by XRF (x-ray fluorescence).

Comparison of different carbon fibers /4

The results of different carbon fibers are shown in Table IV. We analyzed T 300, Celion 3000/6000/12,000, HTS and AS-1. It can be easily seen that the most stable PAN fibers such as Celion G 50 and GY 70 exhibit a high carbon content as well as also a relatively high modulus. In contrast thereto the 240 GN/m^2 modulus materials have a considerably lower carbon content between 91 and 96%. It must be noted that of these materials only the Celion fiber exhibits a low sodium and potassium alkali content. All of the relatively high-stability fibers have a lower alkaline content than the fibers which proved to be more unstable.

Metal traces in precursors

It is assumed that the metals in PAN-based carbon fibers originate in the precursor [4,5]. From Table V it can be seen that the precursor for Celion exhibits a negligible sodium and potassium content, while Courtelle has a relatively high sodium content. Figure II shows that the effect of the precursors on the thermal stability of the fibers, which have a relatively low modulus and which were produced at relatively low temperatures up to ca. 1500° K, is most significant. In this temperature range the Celion-carbon fiber has by far the best properties. For production temperatures of ca. 1850° K the conversion into carbon is nearly complete and the sodium and potassium content is considerably lower, just as for all commercially available high-modulus fibers based on PAN precursors.

4. CAUSES FOR THE INSTABILITY

It is assumed that the stability of the Celion fiber is directly connected with the low alkali content in the fiber. It is known that sodium and potassium act as catalysts for the oxidation in air [6]. Actually in-house investigations of carbon fibers temperature-aged in air have shown that sodium impurities lead to large local craters on the surface of GY 70, if the fiber is subjected to 900° K in air. In order to prove the mechanism of this oxidative decomposition of carbon fibers, samples of T 300 and Stackpole, both fibers with relatively high sensitivity /5 toward oxidation, were subjected to average conditions which caused a significant, but not complete erosion. The conditions were 653° K for 24 hours in air. Subsequent measurements showed a loss of weight of 24 or 75% for the Stackpole or T 300 fibers. Nevertheless the fibers were still intact, even after such a pronounced erosion, which we were able to prove through investigations under the electron microscope. The initial and the final tensile strengths were investigated and are shown in Table VI. It was found that, although the strength of the fibers was reduced a small amount, the modulus remained unchanged. It is assumed that this result can be attributed to the catalytic erosion in the presence of alkali, which was uniformly distributed in these fibers. An apparent deviation from this above-mentioned causal relationship was observed on the AS 4 carbon fiber. The loss in weight at 648° K after 24 hours in air is only insignificantly higher than that for Celion despite the high sodium content of ca. 1,000 ppm.

Two possible explanations are:

1. that washing of the finish in hot acetone has no effect (and that the sodium is located in the finish), or

2. that the fiber exhibits an unusually high carbon content of 99%.

These possibilities should be investigated.

5. EFFECT OF FIBER COATINGS

In order to simplify the handling of carbon fibers, it is customary to provide them with a surface finish. Materials are usually applied at about 1% and contain epoxy or epoxy derivatives, in order to guarantee compatibility with this very widely used matrix material. While these finishes do not seem to influence the properties of epoxy resin composite materials, which are employed at temperatures of 450° K or less, one must assume that they exert a harmful effect on the properties of composite materials, whose hardening cycle and/or utilization temperature reach 450° K. Above this temperature the components frequently /6
tend to vaporize or they are unstable and can thus produce gas bubbles or void between fiber and matrix. Tables I and II already showed the effect of loss of weight caused by the finish of the Celion fiber, while Table VII proves that this loss of weight occurred not only in the fiber, but also can be shown in the composite material. The bending- and shear properties, shown in Table VII, do not seem to be particularly affected; however, one must remember that it is just these properties which are less susceptible than the others.

Explanations:

The tensile strength in transverse direction of epoxy-finished Celion/LaRC 160 laminates is only 35 MN/m^2 compared to 70 MN/m^2 of test bodies with polyimide-finished Celion fibers in the same epoxy system (see Tables VIII and IX). The polyimide finish which was originally used for the Celion fiber, is based on DuPont No. 150, a resin system which is no longer available commercially. A substitute resin was developed by the Celanese Co., which combines thermal stability with improved handling characteristics. Thus elementary fiber fractures and fluffing effects were reduced considerably. It is expected that not only the weaving, but also the production of prepregs will be simplified with this new finish. The stability of this finish developed especially for polyimides is shown in Figure III compared to Celion with an epoxy-compatible finish.

6. INVESTIGATIONS WITH COMPOSITE MATERIALS

The excellent thermal oxidative strength of the Celion fiber takes on importance only if composite materials with these fibers and with the use of high temperature resins can be produced. The Celion fiber has a higher oxidative resistance at increased application temperatures than most other available fibers having the same order of magnitude with respect to cost and modulus. The properties of Celion LaRG 16 polyimide composite materials can be seen in Table IX. The test samples were tested at 295° K and 533° K at 0, 200, and 500 hours of temperature-aging in air at 533° K. These fibers contain an epoxy finish and it can be clearly seen that the transverse (90°) tensile strength is rather low, while the remaining mechanical properties are only insignificantly lower than those of the conventional epoxy-based composite materials. The bending- and shear strength at elevated temperatures show a /7
minor increase with increasing temperature effect. This must be most probably attributed to an additional after-hardening process,

which becomes effective during aging. Similar effects were also observed [7] in other investigations.

At this point it seems clear that no disadvantageous effects resulting from fiber stability at 533° K can be expected in composite material with Celion fibers. The data of Table X were produced in order to show the acceptable quality of properties in composite material, which can be obtained with the new PI finish. In particular the 90° bending strength again shows the high quality of properties which can be obtained by the use of a stable polyimide-compatible finish.

7. SUMMARY

It is shown that all high-modulus carbon fibers (345 GN/m^2) have good resistance toward thermal oxidation in air. However, of the more economical and wider distribution materials with lower modulus (240 GN/m^2), Celion exhibits a particularly high oxidative resistance at high temperatures. The difference compared to the other fibers was attributed to the low content of sodium and potassium in the Celion-carbon fiber.

Furthermore it was shown that improved properties in Celion carbon fiber/polyimide systems can be obtained if a fiber with a high-temperature-polyimide-compatible finish is used.

The authors would like to thank Mr. Hector Zabaleta who made most of the tests shown in this report.

REFERENCES

[1] Advanced Composites Design Guide, Vol. IV, Materials.

[2] R.N. Griffin, NASA CR-134987, "Further Development of High Temperature Resistant Graphite Fiber Coupling Agents," March 1976.

[3] P.E. McMahon, "Oxidative Resistance of Carbon Fibers and Their Composites," ASTM STP658, p. 254.

[4] H. F. Mark, S. M. Atlas and E. Cernia. "Man Made Fibers Volume 3", Interscience, New York 1968, p. 168.

[5] Ibid, p. 174.

[6] R. N. Smith, Quarterly Review 13, 287 (1959). P.L. Walker, "Chemistry and Physics of Carbon, Volume 4," Marcel Dekker Inc. (1968), pp. 287-324.

[7] R. D. Vannucci and W. B. Alston. NASA TM X-71816 "PMR Polyimides with Improved High Temperature Performance," February 1976.

Table I

Weight loss of different carbon fibers after 24 hours at 648° K in air

fiber	% carbon	modulus GN/m^2	% weight loss
GY-70	99.3	517	0.1
Celion G50 (no size)	99.7	345	0.2
UCC VSA11 (pitch based)	--	345	0.4
Hercules HMS	--	345	1.6
Celion 3000 (standard size)	93	241	1.7
Celion 6000 (standard size)	93	241	1.9
Celion 6000 (no size)	93	241	0.5
Celion 12,000 (no size)	93	241	0.4
Hercules HTS	--	276	3.4
Thornel 300	91.3	241	14.9
Hercules AS-1	93.9	241	36.5

Table II

Weight loss of different carbon fibers after temperature aging at high temperatures in air /12

fiber types	weight loss in % at 588° K in air after				
	50 hrs.	100 hrs.	200 hrs.	500 hrs.	1000 hrs.
Hercules HTS, no size	0.3	0.9	0.8	1.2	--
Celion 3000, standard size	1.7	2.0	2.8	5.1	7.1
Celion 3000, no size	0.4	0.9	1.5	3.3	--
Thornel 300, 309 size	1.4	3.0	6.5	22.8	49.7
Celion G50, no size	0.4	0.4	0.5	0.6	--

Table III /13

Weight loss of different carbon fibers at 533° K in air

fiber types	percent weight loss after				
	24 hrs.	50 hrs.	100 hrs.	200 hrs.	500 hrs.
Hercules HTS	0.6	0.6	0.7	0.7	0.6
Celion 3000	1.2	1.2	1.3	1.4	1.5
Thornel 300	1.1	1.0	1.2	2.0	4.2

- The Thornel and Celion fibers are provided with a standard finish - while HTS has no finish.

Table IV

Determination of the elements contained in the carbon fibers

fibers	Thornel 300	Gelion 300/6000/ 12,000	Hercules AS-1	Hercules HTS	Celion GY-70	pitch based fiber (UCC)
modulus	241	241	241	276	517	276
% carbon	91.3	93.0	96.6	100	99.3	98.0
% ash	0.7	0.18	0.96	.015	< 0.003	0.1
element (ppm)						
Si	35	144	288	15	< 10	< 10
P	N.D.*	90	N.D.	N.D.	N.D.	< 10
Mg	70	180	96	< 10	< 10	< 10
Fe	N.D.	< 10	48	10	N.D.	< 10
Al	< 10	36	48	10	N.D.	< 10
Ca	35	180	96	15	N.D.	< 10
Na	> 1400	N.D.	2880	30	N.D.	< 10
K	700	N.D.	N.D.	N.D.	N.D.	< 10
Zn	N.D.	90	N.D.	N.D.	N.D.	< 10
XRF						
% S	< 0.05	< 0.05	--	< 0.02	< 0.05	1.8
% Cl	< 0.05	< 0.05	--	< 0.02	< 0.05	< 0.05

- N.D.-not detectable

Table V /15

Elemental analysis of precursors (ppm)

precursor elements	Celion precursor	Courtelle PAN
Na	< 50	2700
K	< 50	< 50
Si	100	50
P	80	N.D.*
Mg	100	40
Ca	150	30
Zn	300	N.D.*

N.D. - not detectable

Table VI /16

Effects of temperature aging at 648° K on selected carbon fibers for 24 hours

carbon fibers	test method	fiber cross-sectional area ($10^{-12}m^2$)	strength (MN/m^2)	modulus (GN/m^2)
Thornel	originally	54.2	2620	269
	after 648° K heat treatment	32.9	2070	269
Stackpole	originally	49.0	2210	220
	after 648° K heat treatment	26.4	2000	220

Table VII

Properties of Celion 6000/LaRC 160 composites at elevated temperatures

		Celion with standard finish				Celion without finish			
			bending strength				bending strength		
aging conditions	test temp. (^{o} K)	% weight loss	strength MN/m^2	modulus GN/m^2	ILSS MN/m^2	% weight loss	strength MN/m^2	modulus GN/m^2	ILSS MN/m^2
starting values	298	--	2150	143	113	--	2160	136	111
	533	--	1670	134	52	--	1600	130	60
200 hours at 533^{o} K in air	533	0.55	1810	139	59	0.33	1600	140	61
500 hours at 533^{o} K in air	533	0.93	1560	141	68	0.57	2080	139	65
1000 hours at 533^{o} in air	533	1.33	1800	138	69	1.08	2070	141	70

Table VIII

Tensile strength, transverse direction and shear strength of LaRC 160 laminates with different finishes

finishes	epoxy finishes	PI finishes
tensile strength in transverse direction (MN/m^2)	35	73
interlaminar shear strength (MN/m^2)	110	111

Table IX

Celion 6000/LaRC 160 aging values at elevated temperatures

properties	hardened		aged in air (533^{o} K) for	
			200 hrs.	500 hrs.
test temp., ^{o} K	298	533	533	533
bending strength MN/m^2	2160	1600	1600	2080
bending modulus GN/m^2	136	130	140	139
0^{o} tensile strength MN/m^2	1850	1780	1920	1780
0^{o} tensile modulus GN/m^2	167	176	181	185
rapid-test shear strength MN/m^2	110	60	61	65
tensile strength in transverse direction MN/m^2	35	17	16	
tensile modulus GN/m^2	11.0	8.3	9.0	

Note: The fibers with epoxy finishes exhibited crack formations at the test samples before ultimate fracture in most cases.

Table X

Properties of Celion 600/LaRc composites and application of fibers with new PI finishes

test temperature, $^{\circ}$K	298	533
0° bending strength, MN/m^2	2080	1470
0° bending modulus, GN/m^2	138	-
90° bending strength MN/m^2	63	47
0° tensile strength MN/m^2	2140	-
0° tension modulus GN/m^2	155	-
0° tension - % elongation	1.4	-
interlaminar shear strength MN/m^2	109	63

ABBILDUNG 1

Figure 1

GEWICHTSVERLUST BEI 588°K IN LUFT. 1. weight loss at 588°K in air

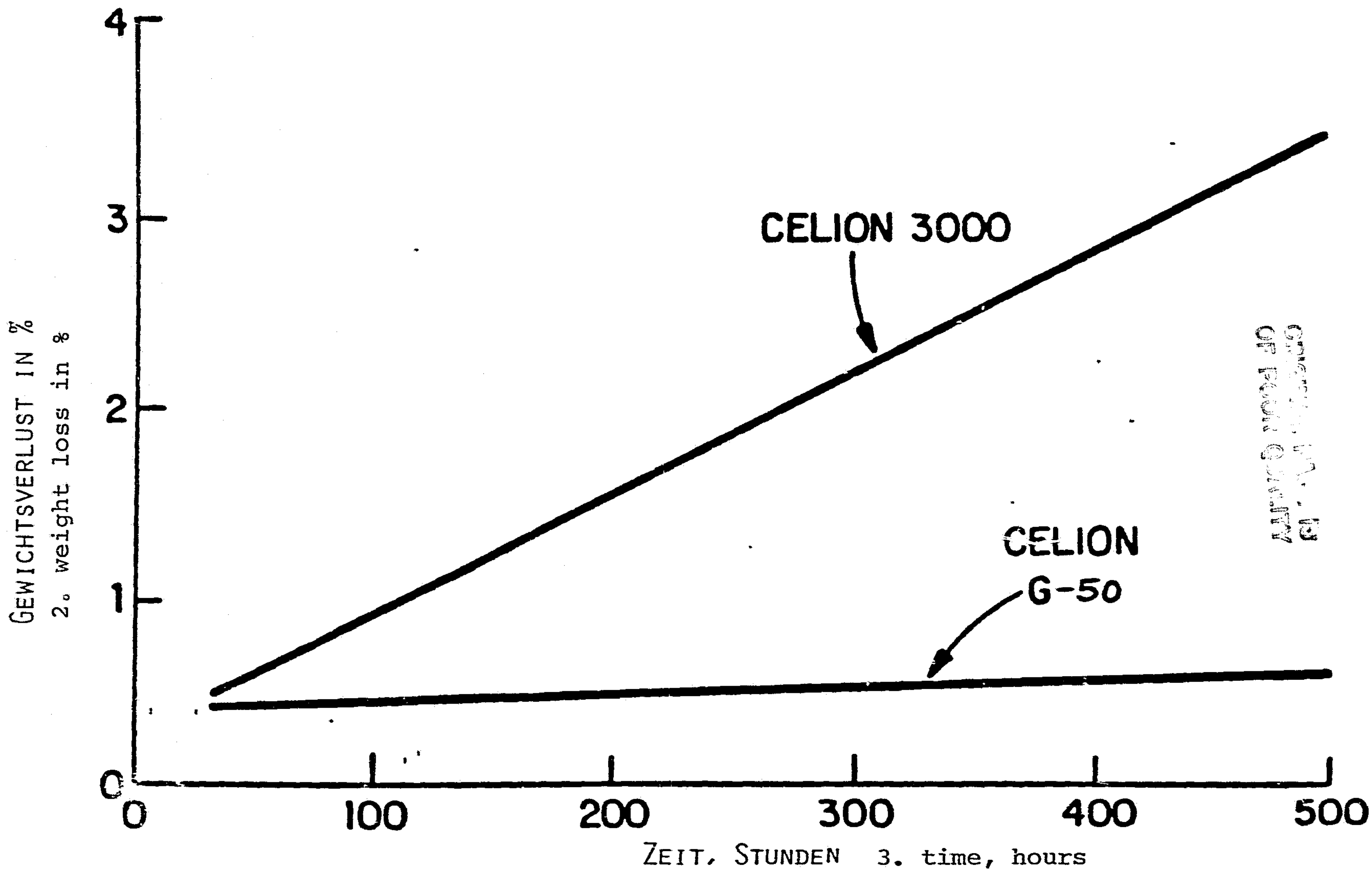

ABBILDUNG 2 Figure 2

1. effect of the precursor on the oxidative stability

DER EINFLUß DES PRECURSOR AUF DIE OXIDATIVE STABILITÄT

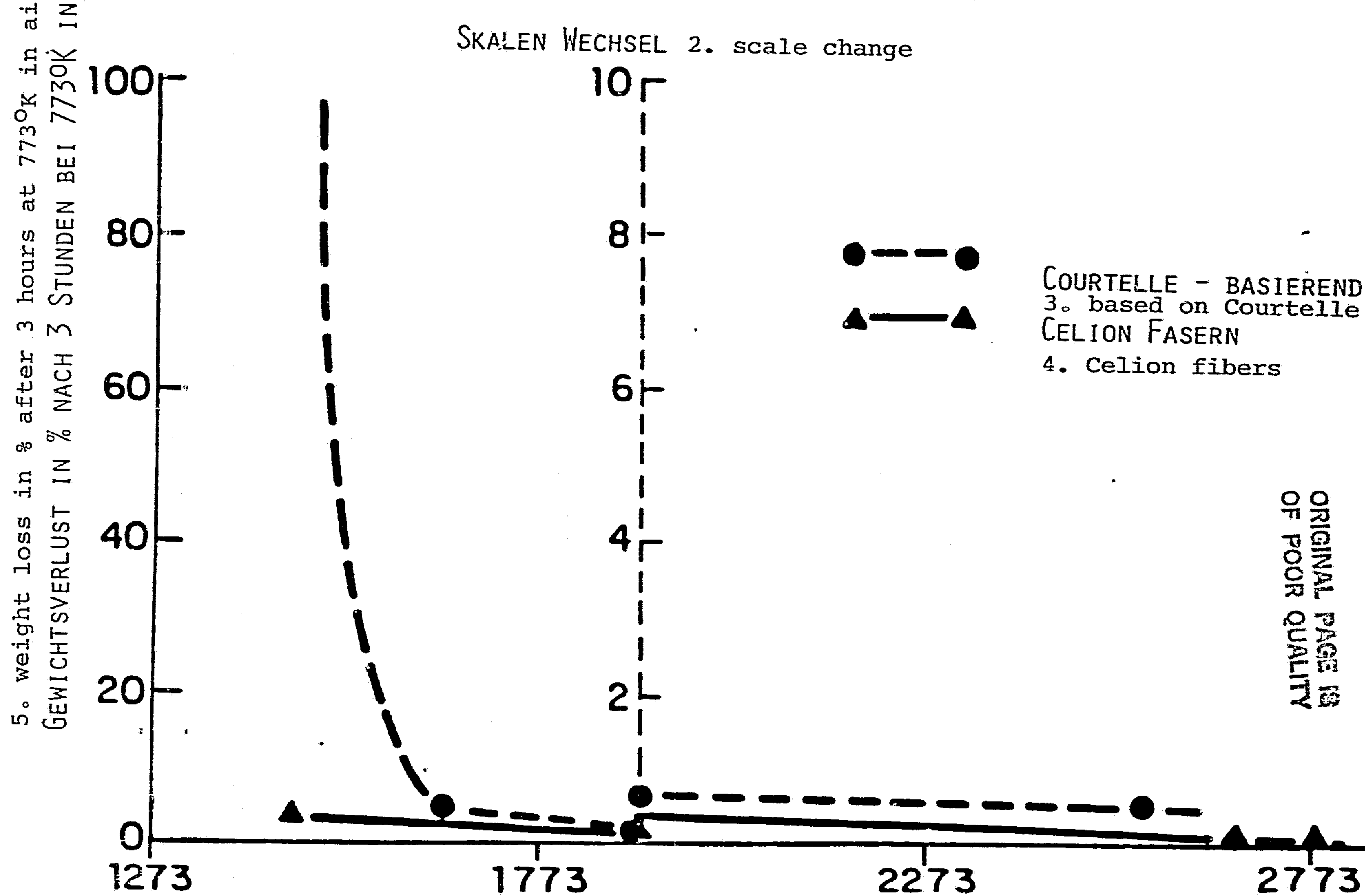

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ABBILDUNG 3 Figure 3

1. weight loss of the carbon fibers at 316°C air as a function of time

GEWICHTSVERLUST DER KOHLENSTOFFASERN BEI 316 °C LUFT

ALS FUNKTION DER ZEIT