Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THERMAL ANALYSIS METHODS FOR THE ESTIMATION OF THERMAL LIFE OF MAGNET WIRE*

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(Received February 26th, 1970)

ABSTRACT

DTA and dynamic and isothermal TG analyses have been performed on a series of commercial magnet wires, in dry oxygen. Good correlations have been observed between the results of each technique and the thermal life ratings of the magnet wire enamels as given by ASTM D-2307. In dynamic TG, correlation is observed between the temperature at 5% weight loss and thermal life rating. Two straight lines are observed, one for low temperature rating enamels, which are primarily aliphatic, the other for high temperature rating enamels, which are primarily aromatic. In DTA, a similar, but less pronounced, breakdown into two curves is seen. Log isothermal rate of weight loss, plotted against reciprocal temperature and extrapolated to 10^{-7}/min, yields a temperature close to the thermal rating temperature. A bimodal distribution is observed in this correlation, also.

The correlations are useful for predicting probable values of thermal ratings for new magnet wire enamels, but cannot supplant the ASTM procedure.

INTRODUCTION

The determination of the thermal life rating of a magnet wire enamel by the customary method, ASTM D-2307[1], is very time consuming, as it requires the maintenance of several wire samples at each of several temperatures and the periodic testing of each sample until electrical failure occurs. The temperatures are chosen so that the time to failure at the lowest temperature exceeds 5000 h. The logarithm of time to failure is plotted against reciprocal absolute temperature and the resultant curve extrapolated to 20,000 h. The corresponding temperature, which we will call $T_{20,000}$, is the thermal rating of the enamel, and customarily delimits the highest permissible temperature of use of the magnet wire.

Several attempts have been made to develop thermal analysis procedures to provide information approximating that given by the ASTM D-2307 method[2-8]. Both TG and DTA techniques have been used. In a recent paper, David[2] showed a

*Presented at the Symposium on Recent Advances in Thermal Analysis, American Chemical Society Meeting, Houston, Texas, U. S. A., February 23–27, 1970.

correlation between the temperature of initial deflection (extrapolated to zero heating rate) of a TG run on magnet wire, and the $T_{20,000}$ of the wire. More recently, we[3] demonstrated correlations between both TG and DTA data, and $T_{20,000}$, for fifteen commercial magnet wires, listed in Table I. In our TG experiments, a thermogravi-

TABLE I

MAGNET WIRE COMPOSITION

No.	*Abbreviation*	$T_{20,000}$	*Wire*
1	PEn	105	Oleoresinous, plain enamel
2	VB/VF	105	Polyvinyl butyral overcoated polyvinyl formal
3	SA	115	Solderable acrylic
4	VF	115	Polyvinyl formal
5	N/VF	115	Nylon overcoated polyvinyl formal
6	MVF	120	Isocyanate modified polyvinyl formal
7	U	120	Polyurethane
8	N/SA	125	Nylon overcoated solderable acrylic
9	N/U	130	Nylon overcoated polyurethane
10	N/E(F)	185	Nylon overcoated Class F polyester
11	EI	200	Polyester–imide
12	EIA	210	Polyester–imide–amide
13	E/E(H)	210	Polyethylene terephthalate overcoated Class H polyester
14	AI/E(H)	225	Amide–imide overcoated Class H polyester
15	I	250	Polyimide

metric analysis is performed on an enameled wire sample in flowing oxygen. The temperature at which 5% of the enamel weight has been lost, T_{TG}, correlates well with $T_{20,000}$, as shown in Table II and Fig. 1.

TABLE II

THERMOGRAVIMETRY RESULTS

	Wire	$T_{20,000}$	T_{TG}	T_{CC}	*Error* (T_{CC})	T_{PC}	*Error* (T_{PC})
1	PEn	105	258	94	−11	112	7
2	VB/VF	105	264	100	−5	114	9
3	SA	115	301	142	27	122	7
4	VF	115	283	122	7	118	3
5	N/VF	115	281	120	5	117	2
6	MVF	120	282	121	1	118	−2
7	U	120	270	107	−13	115	−5
8	N/SA	125	292	132	7	120	−5
9	N/U	130	270	107	−23	115	−15
10	N/E(F)	185	307	149	−36	187	2
11	EI	200	370	220	20	209	9
12	EIA	210	371	221	11	210	0
13	E/E(H)	210	348	196	−14	202	−8
14	AI/E(H)	225	380	232	7	213	−12
15	I	250	505	372	122	259	9

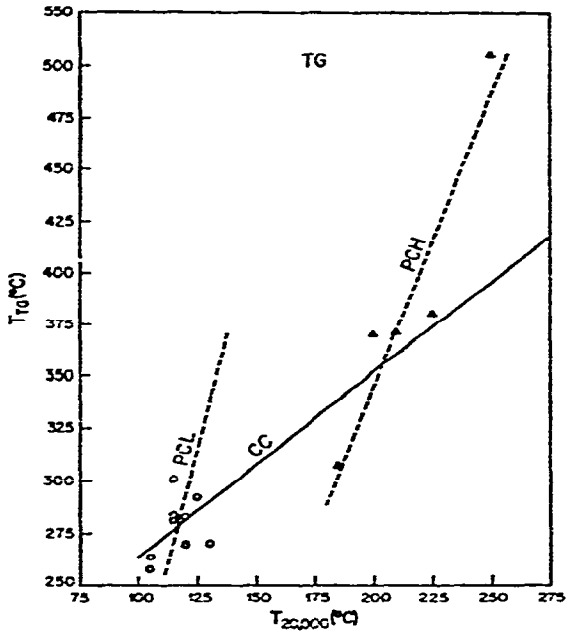

Fig. 1. Temperature of 5% weight loss, T_{TG}, *vs.* ASTM D-2307 20,000-h temperature rating, $T_{20,000}$, for 15 magnet-wire enamels. CC, curve for all enamels. PCL, curve for low temperature enamels. PCH, curve for high temperature enamels.

In Fig. 1, PCL refers to the correlation curve for the lower temperature, aliphatic-based enamels, while PCH refers to the higher temperature, aromatic-based enamels. In the Table, T_{CC} is the value of $T_{20,000}$ that would be predicted from the value of T_{TG} using the complete curve for all the enamels, CC, while T_{PC} is the corresponding temperature from the appropriate partial curve, PCL or PCH.

The DTA experiment involves measurements using a Du Pont Model 900 DTA with the DSC cell attachment. The temperature used, T_{DSC}, is defined by the intersection of the forward extrapolation of the base line and the backward extrapolation of the first major peak occurring at a temperature higher than T_{TG}. T_{DSC} is defined in this way to avoid the interference of small, low temperature peaks which are probably not significant in the enamel deterioration process. The DSC cell was used because thermal contact with the wire specimens was more readily achieved, and because the base line is more uniform than in our DTA cell. The calorimetric capacities of the DSC cell are not utilized; presumably similar results can be obtained with a DTA apparatus.

The results of this procedure are shown in Table III and Fig. 2. In Table III, T_{CC} and T_{PC} have meanings similar to those defined for Table II. As is apparent, the correlation is somewhat better than for the TG results, with the exception of the highest temperature enamel (polyimide), which was not included in the calculation of the correlation curve PCH.

As is evident from Tables II and III, the correlation between $T_{20,000}$ and T_{TG} or T_{DSC} is reasonably good, and the implication is that $T_{20,000}$ for a new enamel

can probably be predicted to within 10 °C by either method. However, the prediction is not yet sufficiently reliable so that a new magnet wire can be safely used without the long-term ASTM D-2307 testing, as evidenced by our polyimide results, and by those of Schweitzer and Strugar[9]. In order to begin to develop a theoretical basis for the prediction of $T_{20,000}$, rather than depend entirely on empirical correlation, we have measured, and report in this paper, the rates of isothermal weight loss and hence, an energy of activation for the initial decomposition.

TABLE III

DIFFERENTIAL SCANNING CALORIMETRY RESULTS

	Wire	$T_{20,000}$	T_{DSC}	T_{CC}	*Error* (T_{CC})	T_{PC}	*Error* (T_{PC})
1	PEn	105	186	58	−47	95	−10
2	VB/VF	105	222	96	−9	108	3
3	SA	115	248	122	7	118	3
4	VF	115	250	125	10	119	4
5	N/VF	115	254	128	13	120	5
6	MVF	120	254	128	8	120	0
7	U	120	258	133	13	122	2
8	N/SA	125	261	136	11	123	−2
9	N/U	130	268	143	13	125	−5
10	N/E(F)	185	285	160	−15	184	−1
11	EI	200	315	192	−8	201	1
12	EIA	210	336	213	3	213	3
13	E/E(H)	210	334	211	1	211	1
14	AI/E(H)	225	356	234	9	223	−2
15	I	250	520	404	154	315	65

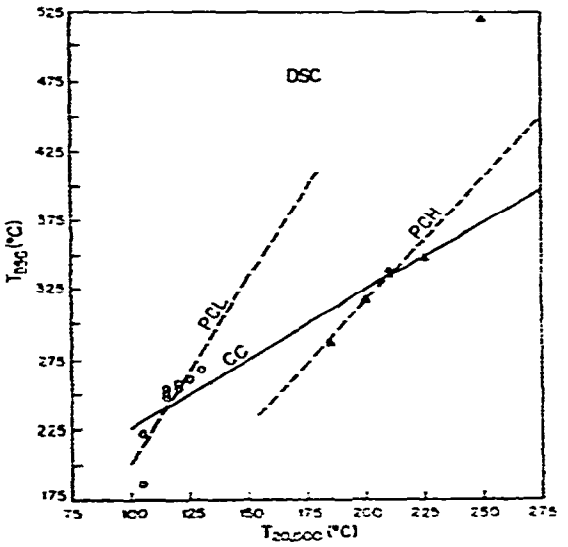

Fig. 2. Extrapolated initial DSC temperature, T_{DSC}, *vs.* ASTM D-2307 20,000-h temperature rating, $T_{20,000}$, for 15 magnet-wire enamels.

EXPERIMENTAL

Isothermal TG runs were made, using a Du Pont Model 900 DTA–Model 950 TG Analyzer, and also a Fisher Series 100 TG System. Runs at low rates of loss were done with the Fisher system because of higher sensitivity, and because a strip chart recorder is more convenient for long runs. Results at high rates of loss were similar for the two sets of apparatus. All runs were performed in oxygen flowing at 100 cc/min.

The samples were AWG No. 18 (1.02 mm diameter) heavy build (0.032 mm enamel) copper magnet wire except for the plain enamel (PEn), which was single build (0.016 mm enamel). In order to maintain the interaction between the enamel and the wire, the enamel was left on the wire during the runs. Sample size was approximately 100 mg, of which approximately 2% was enamel, except for plain enamel (1.2%). The wires used are listed in Table I, together with $T_{20,000}$ and with abbreviations for identification of the wires in other Tables.

RESULTS AND DISCUSSION

The weight of enamel on a 100 mg sample of 18H (*i.e.*, 18 gauge, heavy build) magnet wire is 2.0 $\pm$0.2 mg. Isothermal rates of weight loss were measured when 5% of this amount, or 0.1 mg, had been lost. David[2] has demonstrated that the weight loss follows zero order kinetics. Therefore, a plot of ln dw/dt against $1/T$ should give a straight line, with slope $-E/R$, where E is the activation energy. The units used for dw/dt are a matter of convenience, since in the zero order case the rate constant, k, is given by $k = c\,dw/dt$, where the constant c can transform the units used to a theoretically more significant set. Taking logarithms, we see that $\ln k = \ln c + \ln dw/dt$, and the slope of ln dw/dt against $1/T$ will be independent of the value of c and the units used. Herein, weight-loss rates are recorded in terms of fraction of total sample per minute.

For each enamel, from five to seven isothermal runs were made. The measured rates, dw/dt, were analytically fitted by means of least squares to an equation of the form $\ln dw/dt = m/T + b$. The correlation coefficients fell between -0.950 and -0.993, with the exception of enamel 14, AI/E(H), for which $r = -0.909$. Some representative curves are shown in Fig. 3.

From inspection of the extrapolations of the plotted data, it is observed that the $T_{20,000}$ values for several of the enamels fall close to $dw/dt = 10^{-7}$ mg/mg/min. The high temperature enamels group around 2.3×10^{-7}, while the low temperature enamels average 5.3×10^{-8}. In both cases, enamels far from the average were omitted in calculating the average values. For a particular enamel, we define T_{ISO} as the temperature calculated by inserting 2.3×10^{-7} or 5.3×10^{-8}, as appropriate, in the least squares equation for that enamel. The data are presented in Table IV.

With this correlation, a new method is available for the estimation of $T_{20,000}$ for a new enamel. A comparison of the closeness of fit of the values of $T_{20,000}$

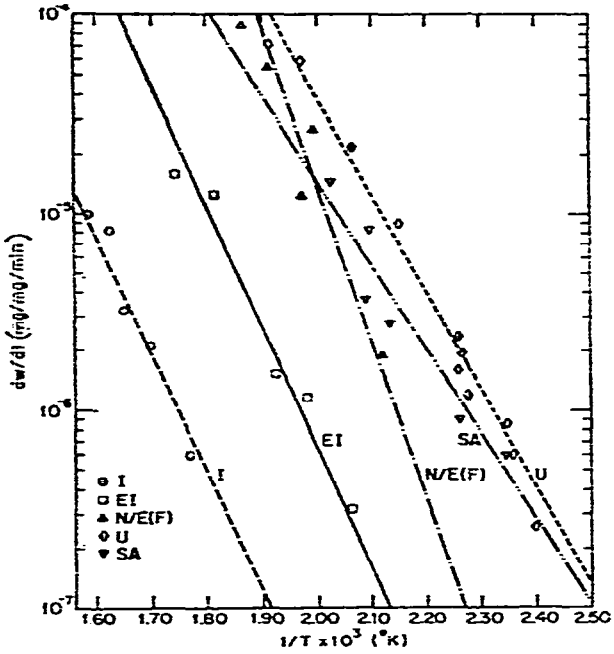

Fig. 3. Isothermal rate of weight loss *vs.* reciprocal absolute temperature, for 5 magnet-wire enamels.

TABLE IV

ISOTHERMAL WEIGHT LOSS MEASUREMENTS ON MAGNET-WIRE ENAMELS

Enamel		$T_{20,000}$	T_{iso}	E(kcal/mol) ($= -mR$)	b	$dw/dT \times 10^8$ at $T = T_{20,000}$
Low temperature enamels						
1	PEn	105	123	26.0	16.01	1.1
2	VB/VF	105	104	19.6	9.18	5.6
3	SA	115	118	20.0	9.05	6.5
4	VF	115	115	23.0	13.09	5.2
5	N/VF	115	104	20.0	9.94	12
6	MVF	120	125	26.0	16.07	3.3
7	U	120	116	23.1	13.13	6.9
8	N/SA	125	122	22.4	11.74	6.5
9	N/U	130	112	22.6	12.85	20
High temperature enamels						
10	N/E(F)	185	175	34.9	23.95	56
11	EI	200	206	25.8	11.83	17
12	EIA	210	210	28.9	14.90	24
13	E/E(H)	210	207	34.7	21.06	29
14	AI/E(H)	225	207	23.2	9.27	70
15	I	250	268	29.6	12.26	8.7

produced by the three techniques, TG, DSC, and isothermal, is shown in Table V. It is evident that the TG and DSC techniques give somewhat less scatter than does the isothermal method. It is interesting to note that the enamels that give the poorest

results in either the TG or DSC techniques also give the poorest results with the isothermal method.

TABLE V

COMPARISON OF PREDICTION RESULTS

	Enamel	$T_{20,000}-T_{TG}$	$T_{20,000}-T_{DSC}$	$T_{20,000}-T_{ISO}$
1	PEn	7	−10	18
2	VB/VF	9	3	−1
3	SA	7	3	3
4	VF	3	4	0
5	N/VF	2	5	−11
6	MVF	−2	0	5
7	U	−5	2	−4
8	N/SA	−5	−2	−3
9	N/U	−15	−5	−18
10	N/E(F)	2	−1	−10
11	EI	9	1	6
12	EIA	0	3	0
13	E/E(H)	−8	1	−3
14	AI/E(H)	−12	−2	−23
15	I	9	65	18

Energies of activation, calculated from the isothermal data, are listed in Table IV. No correlation has been observed between energy of activation and either $T_{20,000}$, or the deviation of any of the predicted values, T_{TG}, T_{DSC}, or T_{ISO}, from $T_{20,000}$. In general, the energies calculated for the low temperature enamels are lower than those for the high temperature enamels, although there is some overlap. Further, there is only partial correlation between the activation energy calculated from the isothermal data and that calculated by David[2] from TG data, the correlation being between some of the low temperature enamels. There was no correlation between the isothermal energies of activation and those calculated from our TG data, using an approximation due to Doyle[10]. Doyle's equation 4-68 reduces to:

$$E \cong 20(-\mathrm{d}h/\mathrm{d}t)RT^2$$

for zero order kinetics at five percent weight loss. The assumption of zero order kinetics may not be valid, as the reaction(s) are complex, particularly at the start of the decomposition. In this regard, Otis and Young[11] have pointed out that the initial decomposition for several enamels seems to be the disappearance of residual functional groups, followed by a more uniform chain decomposition.

It must be emphasized that these correlation techniques cannot be used to replace ASTM D-2307 procedures. Enamels and enamel–varnish combinations have been found which give highly non-linear ASTM D-2307 curves[9,12]. It was shown[9] that TG experiments cannot distinguish the anomalous enamels from the others. In the case cited, the anomaly was due to a transition from crystalline to amorphous

structure. Another problem is the interaction of the enamel with the wire surface. Schweitzer[13] has pointed out that, in the case of polyimide on copper, enamel failure is usually due to interaction of the enamel with the copper. This effect may account for the large discrepancy of the polyimide result in our DSC tests. Refinement and extension of the techniques described are needed before these types of anomalous behavior can be detected by thermal analysis methods.

Extensions of the technique under study in our laboratory include examination of magnet wires by thermo-mechanical analysis (TMA) to determine if anomalous transitions can be detected. Studies of the influence of metals and metal oxides on the decomposition of magnet wire enamels are also under way. The influence of reactive and of non-reactive gaseous environments on the value of T_{TG} and of T_{DSC} has been reported[3]. The change in T_{TG}, due to the presence of a gas, shows promise as a measure of the suitability of the enamel under investigation for service in that environment.

Refinements of the technique being studied include examination of some of the techniques of calculation cited by Doyle[10]. In particular, the time necessary to achieve a certain value of weight loss in an isothermal experiment is interesting. Accurate measurements of elapsed time at temperature were not possible with our present apparatus (Fisher) because of the long equilibration time. A system designed to achieve rapid temperature equilibration is being assembled, which will allow examination of the relationships involving "time to failure".

It should be noted, however, that the extrapolated rate of weight loss at $T_{20,000}$ yields calculated elapsed times of one to three orders of magnitude smaller than 20,000 h. This is not entirely unexpected, since Otis and Young[11] presented data showing considerable weight loss (2–10%) for several magnet wires aged at temperatures equal to or below their thermal rating for periods of 2,000 h or less.

The present techniques have been developed on a strictly empirical basis in order to ascertain whether useful predictions of long term results could be derived. Up to this point, very little attention, beyond speculation, has been focussed on parameters which, intuitively, could affect the correlations and which, if taken into account, could increase their effectiveness.

For example, chemical structure of the enamel would obviously be expected to influence the results of these studies. This is borne out in the observation that two distinct divisions of data are needed in all three of the predictive tools; the basically aliphatic *vs.* basically aromatic classes. In addition, it is to be noted that in the isothermal techniques, the largest discrepancies ($T_{20,000}$–T_{ISO}) are obtained with those resins in which the enamel or enamel top coat is a thermoplastic (uncrosslinked) polymer. For example, nylon top-coated enamels have a T_{ISO} consistently lower than expected by about ten degrees.

The present usefulness of the several techniques described lies in two areas. First, the techniques can be used to provide a rapid estimate of the probable result of ASTM D-2307 testing. This is of use to synthetic polymer chemists engaged in magnet wire enamel development. Second, in quality control, when deviations from

a norm (*i.e.*, in T_{TG}) established for a particular enamel are observed, corresponding variations in the quality of the magnet wire being produced can be expected. There is at present no other rapid way of detecting variations in thermal stability of magnet wire.

ACKNOWLEDGMENTS

We thank Essex International, Inc. for its support of this work and for supplying the magnet wire used. We also thank Dr. R. B. Young for several stimulating discussions.

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