ANALYSIS OF ELASTOMER VULCANIZATE COMPOSITION BY TG-DTG TECHNIQUES

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SUMMARY

Two common problems in the TG-DTG analysis of unknown elastomer vulcanizates and probable solutions are discussed. The first problem concerns the difficulty in quantitatively determining the oil and elastomer in the compound in cases where their volatilization temperature range overlaps. After a review of the published works which studied this problem, isothermal TG (with or without vacuum) along with the use of "High Resolution" TG equipment is recommended.

The second problem concerns separate determination of carbon residue from the elastomers and added carbon black in the compound, which very often oxidizes together. Subtraction of the carbon residue formed by the elastomers, determined by previous analyses, from the total weight loss in oxygen, was suggested in the literature. However, the quantity of char depends on type of the elastomer, as well as its concentration, curative type and amount and rate of heating. The problem is not, therefore, fully resolved. Experiments under slow feed of lean oxygen gas and isothermal temperature were also suggested in the literature. Under this condition, oxidation of carbon black and char may occur at slightly different temperatures and overlapping is minimized. However, this could be achieved only for large and medium particle size blacks (soft blacks) which oxidize at higher temperatures and not for the smaller particle size blacks, (used mostly in tire treads). Further work under slow feed of lean oxygen with a superimposed isothermal program and/or vacuum is recommended. The capability of the recently announced "High Resolution Thermogravimetric Analyzer" should also be explored.

INTRODUCTION

Analysis of elastomer vulcanizate composition is often an important quality control requirement for the rubber industry. Practical rubber formulations are complex mixtures of polymer(s), filler(s), oil, plasticizer, curatives, antioxidants(2), antiozonant(s), and processing aids. The classical ASTM method[1] takes too long to analyze this complex mixture to be of much practical use on a routine basis. It is also costly and very often requires preliminary identification of the polymer type.

Thermogravimetry (TG) is currently gaining wide acceptance as a method for compositional analysis of vulcanizates. The recent ASTM symposium on "Compositional Analysis by Thermogravimetry"[2] attests to this observation. Thermogravimetric analysis not only permits the analysis to be completed in a short time but also requires a small sample.

The first examples of using TG to analyze polymeric materials are found in the work of Chiu[3], Maurer[4,5], and Coats and Redfern[6]. Swarin and Wims[7] made a special effort to accurately determine the oil content of vulcanizates, which often volatilize with the elastomer, and proposed simultaneous use of the derivative thermogravimetry (DTG) curve. Excellent precision and good accuracy were also reported by Maurer[8] for a series of vulcanizates of single elastomers based on ethylene-propylene-diene rubber (EPDM), isobutylene-isoprene rubber (IIR), chloro-isobutylene-isoprene rubber (CIIR), and natural rubber (NR). Harris[9] used the TG method for quality control of carbon black masterbatches of styrene-butadiene rubber (SBR) and butadiene rubber (BR), including oil-extended materials. Leyden and Raab[10] analyzed a formulation based on SBR. The potential of the TG-DTG procedure for quantitative analysis of vulcanizates based on binary elastomer blends was also treated by Maurer[11,12] for EPDM-NR blends and by Brazier and Nickel[13] for natural rubber-synthetic isoprene rubber (IR), NR-BR, and NR-SBR blends. Wide acceptance of the method resulted in an ASTM test method in 1987 entitled, "Compositional Analysis by Thermogravimetry"[14]. An International Standard Organization (ISO) method is also under development[15].

Several factors can contribute to interference with this simple TG-DTG procedure[16,17]. One factor is overlap of the process oil, resin etcetera. with the polymer decomposition region. The second, by far the greatest complication, is observed for the elastomers with a heteroatom in the monomer, e.g., acrylonitrile-butadiene rubber (NBR), chloroprene rubber (CR), poly(vinyl chloride) (PVC), chloro-sulfonated poly(ethylene) rubber (CSM, Hypalon), poly(acrylates) (ACM), fluoro elastomers (FKM), epichlorohydrin polymer (CO), epichlorohydrin-ethylene oxide copolymer (ECO) etc. These polymers leave a char (carbon residue) after degradation in nitrogen, making it difficult to estimate either the elastomer or carbon black included in the recipe. The purpose of this review is to discuss the procedures that have been suggested to remedy these apparent inadequacies of the TG-DTG method.

DTG curves for elastomers have also been used as "fingerprints" to identify many single elastomers and blends[16]. Quantitative determination of the ratio of elastomers[12,17] has also been attempted from DTG peak heights[11, 13, 18]. In order to focus our attention to the compositional analysis of the vulcanizates, these other capabilities of DTG have been precluded from this discussion.

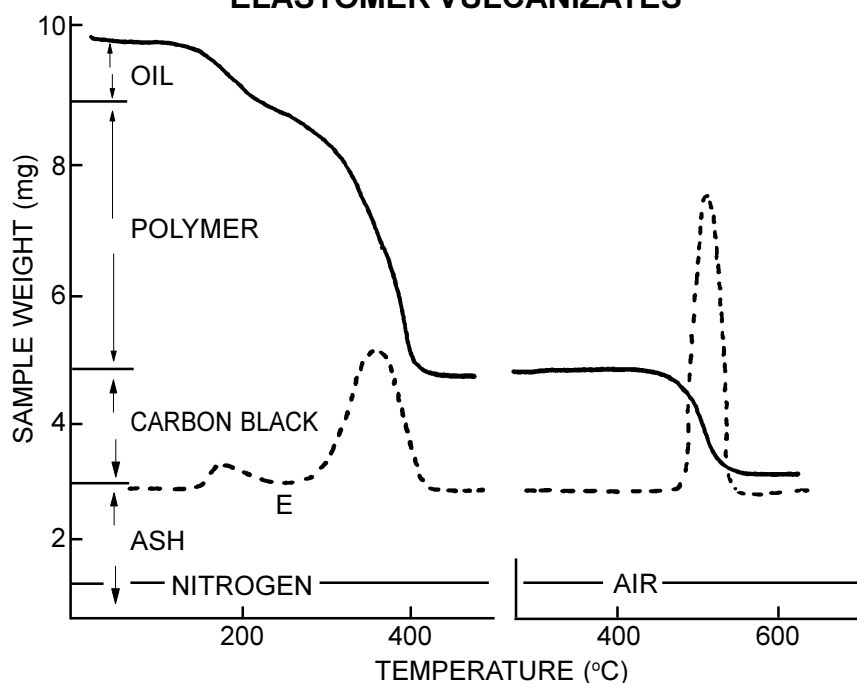## SCHEMATIC TG AND DTG CURVE OF ELASTOMER VULCANIZATES[19]

Figure 1

Table 1
DEFINITIONS OF DIFFERENT FRACTIONS IN THERMOGRAVIMETRIC ANALYSIS OF ELASTOMERS

Highly volatile matter	Refers to moisture, polymer, diluent, oil, plasticizer, emulsifiers (e.g. in styrene-butadiene rubbers), curatives (sulfur, accelerator), antioxidants, antiozonants, and other low boiling components (approx. 300°C or lower)
Medium volatile matter	Refers to medium volatility material such as processing oil, processing aid, elastomer, resin (used as a curing agent) etc. In general, these materials degrade at 300 to 750°C.
Combustible material	Refers to oxidizable material, not volatile (in the unoxidized form) at 750°C or some stipulated temperature dependent on the material (e.g., carbon black, graphite, etc.).
Ash	Refers to nonvolatile residues in an oxidizing atmosphere which may include metallic oxides, filler or inert reinforcing material (e.g. silica). In the absence of nonblack fillers, the ash is composed of zinc oxide which is a component in most vulcanizates. A small amount of ash (<1%) may be due to elastomer residue.

EXPERIMENTAL

A schematic TG-DTG curve of elastomer vulcanizate analysis is shown in Figure 1 to illustrate the procedure[19]. The standard test method for compositional analysis by TG[15,20] describes a general technique to determine the quantity of four arbitrarily defined components - 1) highly volatile matter, 2) matter of medium volatility, 3) combustible material, and 4) ash left after oxidative decomposition of inorganic components. The components filling this description in the case of elastomer vulcanizates are shown in Figure 1 and Table I. The definitions of the four components are based on their relative volatility or lack of it. The success of the method depends on the differing thermal stability ranges for each component in an inert and an oxidizing atmosphere.

The analysis is performed by first taring the electrobalance, introducing and weighing the specimen, and establishing the inert atmosphere. The desired heating program is then initiated while the specimen mass is continuously monitored by a recording device. The mass loss profile may be expressed in either milligrams or percent of the original sample mass. Once the medium volatile matter mass loss plateau is established, usually at 600°C or above, the atmosphere is changed from inert to oxidative. In the case of elastomer vulcanizates, the sample is often cooled to 400°C in
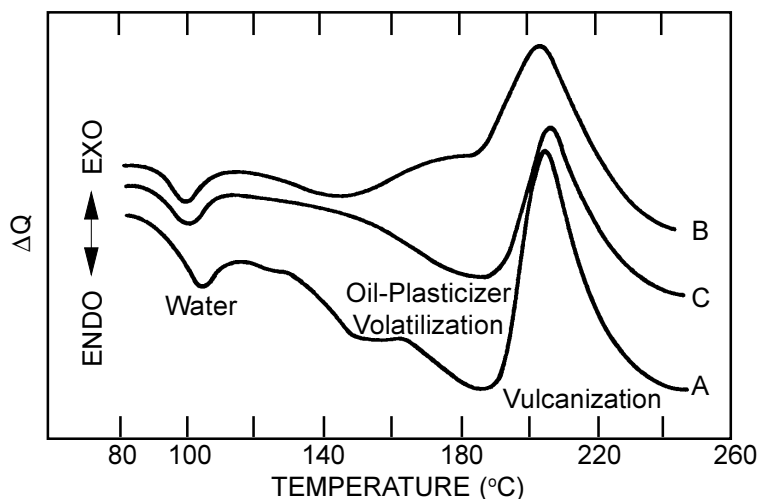
DSC SCANS OF TIRE STOCKS AT 20°C/MIN

Figure 2

nitrogen before changing to an oxidative atmosphere, since many carbon blacks oxidize below 600°C. This modified procedure often allows identification of carbon blacks from DTG peak temperatures[5,12]. The analysis is complete when mass loss plateau corresponding to the final sample mass is established. The method encompasses all commercial and specially designed thermogravimetric analyzers capable of temperature programming while continually weighing the sample under atmospheric control. Specimens are generally solid (but may be liquid, e.g. latex) and are generally 10 to 20 mg in size. Selection of test parameters includes a modular approach using a combination of optimal heat and hold periods. The smaller sample size provides better resolution of the curves and can be more advantageously used with more recent instruments which have better sensitivity. The use of small sample size and low heating rate have been stressed by several reviewers[6,21,22]. A higher conductivity purge gas (helium) has also been claimed to be helpful.

RESULTS AND DISCUSSION

Determination of "Highly Volatile Matter"

A. Moisture and Process Solvent - Table I shows that the "highly volatile matter" may contain a low boiling fraction consisting of moisture, polymer-diluent, etc. Analysis of water and process solvents could best be accomplished by holding the sample at an isothermal condition under inert atmosphere and possibly under reduced pressure, as a first step in the TG procedure. This analysis may also be accomplished and facilitated by the use of the DSC curve[23] (Figure 2).
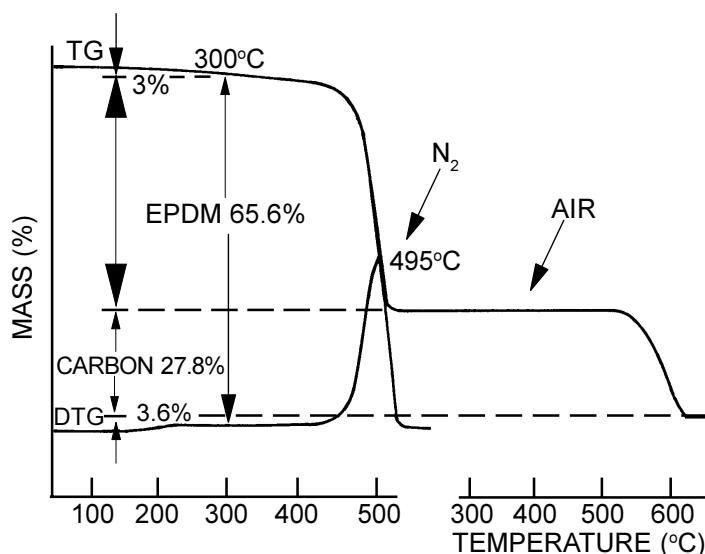
TG-DTG CURVES OF EPR VULCANIZATES

Figure 3
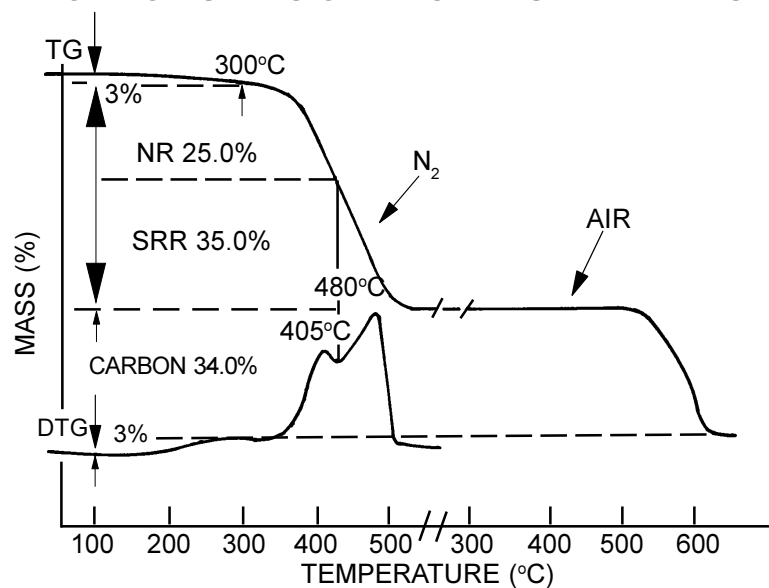
TG-DTG CURVES OF NR-SBR VULCANIZATES

Figure 4

B. Curatives and Antioxidants - Other components mentioned in Table I under "highly volatile matter" are the curatives (excess sulfur, accelerator, emulsifiers (e.g. in SBR) and the antioxidants). Relatively little note has been taken of the analysis of these low molecular weight organic components which are almost always volatilized under 300°C and included under "oils and plasticizers". Jaroszyn' ska and Kleps[24] show a small discontinuity at 300°C in the TG-DTG curves of ethylene-propylene rubber (EPM) and NR-SBR before volatilization of oil at 350°C (Figures 3 and 4). They ascribe the initial decrease in mass to the loss of excess curatives and organic antioxidants. As is evident from Figures 3 and 4, the exact separation of the decomposition ranges of these two groups, even with the use of DTG, is very difficult. Comparatively better results may be obtained by using the graphical method of Swarin and Wims[7], to be described later. In mixes which do not contain oil, the quantity of compounding ingredients may be determined up to the decomposition temperature of 300°C. This, however, requires a previous knowledge of the polymer type.

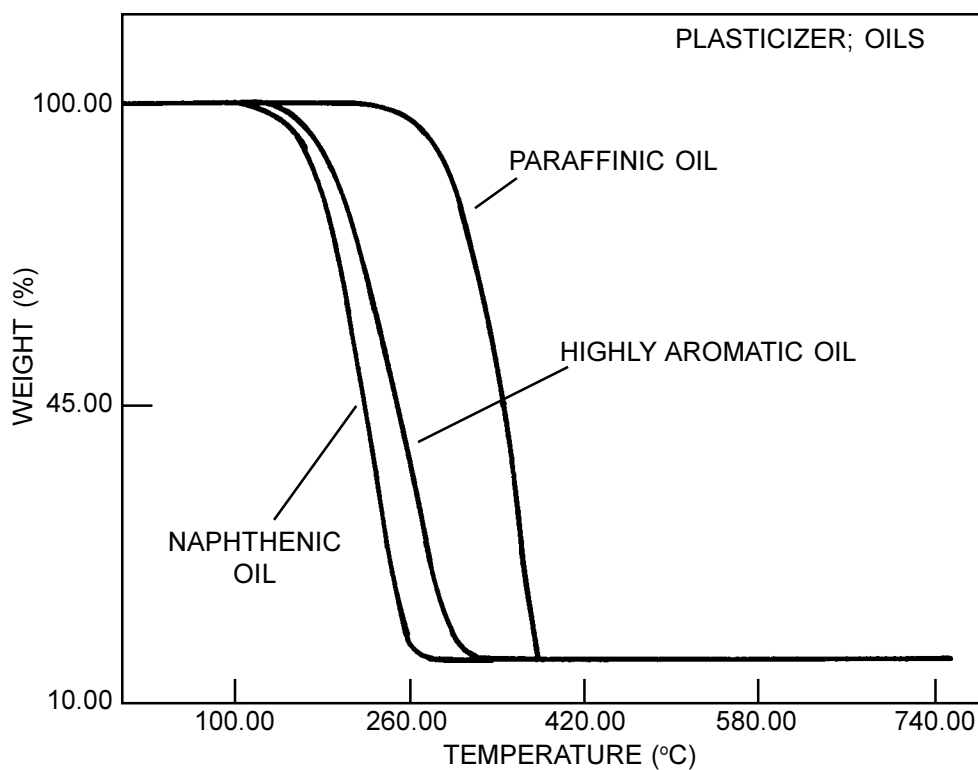## VOLATILIZATION RANGE OF PLASTICIZER/OIL IN NITROGEN

Figure 5

TABLE II

VOLATILIZATION/OXIDATION TEMPERATURE OF DIFFERENT COMPONENTS IN TG-DTG EXPERIMENTS[25]

Constituent Material	Temperature in °C			Atmosphere gas
	Initial	Median	Final	
Napthenic Oil	205	253	300	Nitrogen
Highly Aromatic Oil	250	295	340	Nitrogen
Paraffinic Oil	342	381	420	Nitrogen
Chlorobutyl Rubber	352	395	437	Nitrogen
Natural Rubber (SMR-5)	385	408	430	Nitrogen
Chloroprene Rubber	372	441	510	Nitrogen
SBR	445	473	500	Nitrogen
EPDM	480	490	500	Nitrogen
Carbon Black (N-339)	540	545	550	Oxygen
Carbon Black (N660)	545	550	555	Oxygen
Calcium Carbonate	-	825	-	Nitrogen/Oxygen
Graphite	-	800	-	Oxygen

C. Oil and Plasticizer - As mentioned before, a major challenge in the TG-DTG analysis of elastomer vulcanizates is to accurately assay oil/plasticizer and the polymer, which often show overlapping TG curves. Figure 5 is a collection of TG volatilization curves for three typical plasticizers[25]. Most of these materials have volatilization ranges rather than discrete volatilization points because they are chemical blends of various molecular weights of different volatility. Figure 6 is a collection of TG-volatilization curves for three typical elastomers[25]. Table II lists the initial, median and final temperatures of several representative samples of elastomers, carbon blacks, graphite, and calcium carbonate. It is evident from Figures 5 and 6 and Table II that overlapping of the oil and elastomer TG curves is highly probable, especially if the oil belongs to the less volatile paraffinic type. Many other process oils, plasticizers and processing aids decompose similarly at a high temperature along with the elastomer.

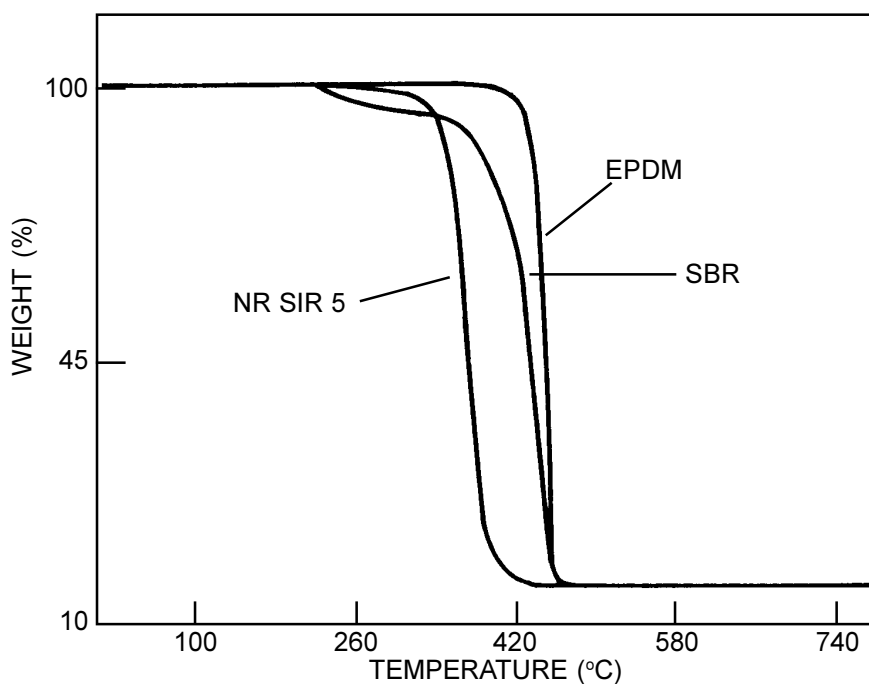**VOLATILIZATION RANGE OF ELASTOMERS IN NITROGEN**

Figure 6

CHARACTERISTICS OF OIL LOSS REGIONS
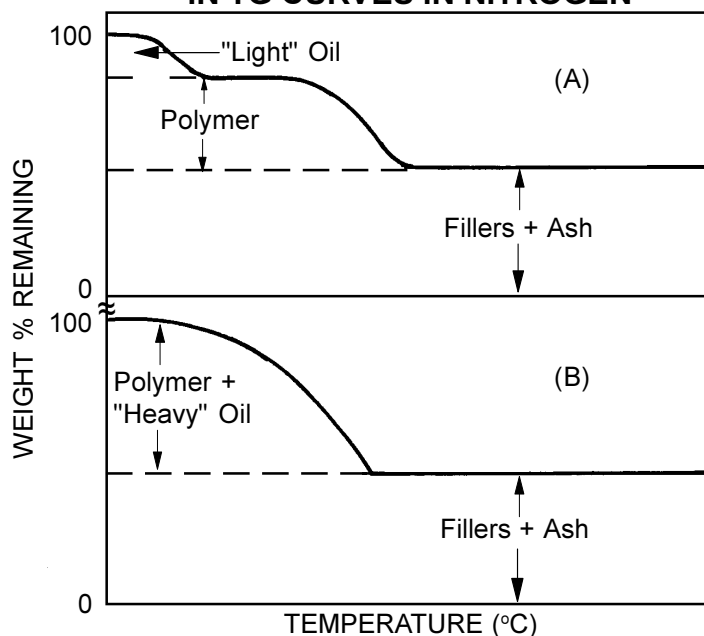## IN TG CURVES IN NITROGEN

Figure 7

Curve B of Figure 2 includes a resin curing agent which degrades along with the polymer. In this case, a portion of the elastomer is decomposed before the complete removal of oil fragments and neither the oil nor the polymer can be accurately determined by a single dynamic TG-DTG curve. The TG curves of "light oil" and "heavy oil" in a typical polymer, presented in Figure 7, show a sharp break between the "polymer" and "light oil" TG curves and no discernible break between the "polymer" and "heavy oil" curves.

Swarin and Wims[7] suggest three methods to resolve this problem in the case of EPDM vulcanizates; these are illustrated in Figure 8. Their three approaches are 1) overlay the TG curve of an unextended elastomer obtained at the same experimental conditions as the oil-extended sample; 2) use a graphical extrapolation technique based on the intersection of the linear regions of the TG curves due to oil only and polymer plus oil; and 3) use the minimum of the simultaneous DTG curve to determine when the oil loss is complete.

**METHODS FOR THE
DETERMINATION OF OIL
AND POLYMER IN EPDM
RUBBER BY TG.**

**A. OVERLAY METHOD
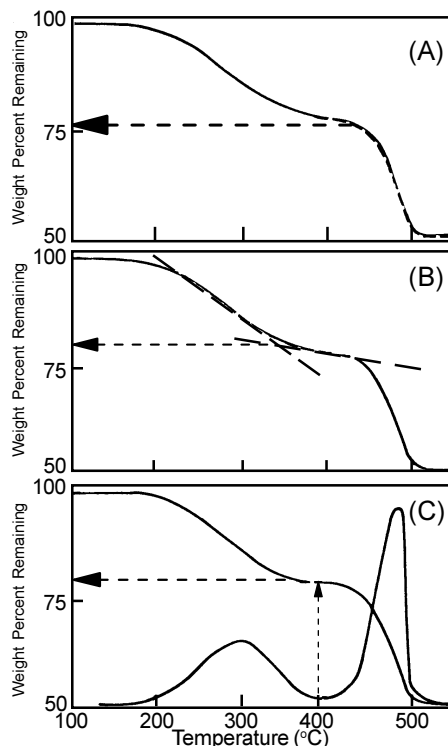B. EXTRAPOLATION METHOD
C. DERIVATIVE METHOD**

Figure 8

Both methods 1 and 3 showed excellent agreement with the known values in the case of EPDM rubber which decomposes at a higher temperature than the unsaturated diene rubbers (NR, SBR, and BR). The extrapolation method (method 2) was not satisfactory for the heavier oil even for EPDM. However, method 1 requires a knowledge of the elastomer type as well as the experimental conditions for cure. It also requires extra work for graphical extrapolation. Increased stability of the elastomers on cure[27] may also add to the complication. Artemov et al.[28] reports that the volatilization temperature for dibutyl phthalate plasticizer depends on the nature of the curative. These considerations make the value of method 1 doubtful for analysis of an unknown vulcanizate. Thus, method 3 is the preferred method. However, resolution of the TG-DTG curves of many practical vulcanizates are not quite as good as shown in Figure 8, making the location of the minimum in DTG curve rather subjective. An example for a SBR track pad rubber formulation for the Army[29,30], is shown in Figure 9.

TG-DTG ANALYSIS OF A SBR VULCANIZATE

Figure 9
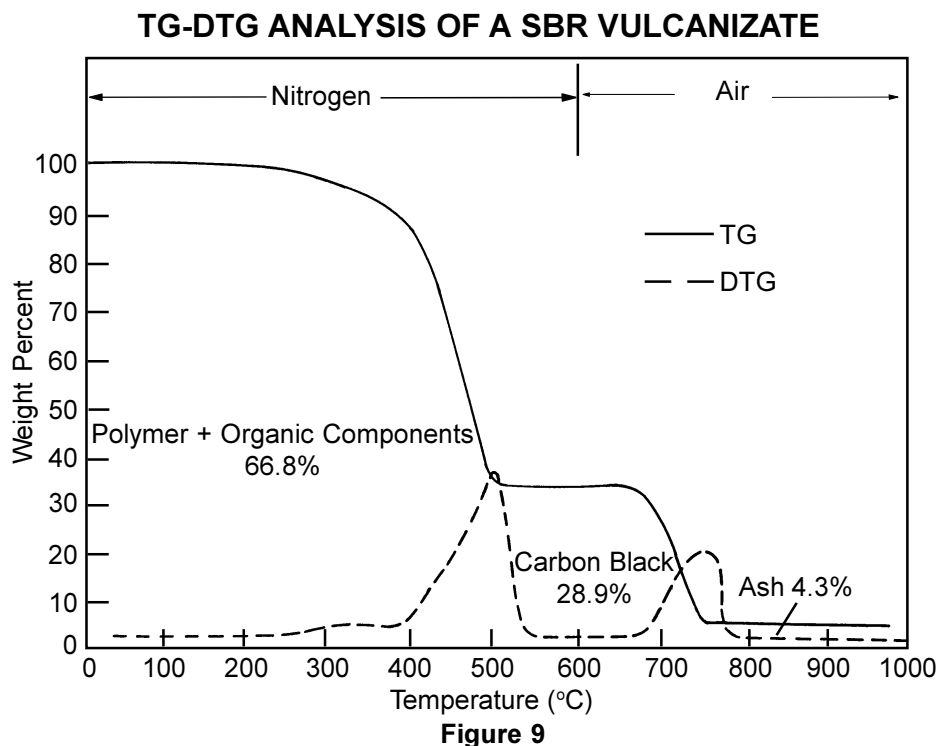
Additional suggestions in early work by Maurer[4] were as follows:

1. Extract the sample to remove oil, excess curatives, etc., prior to TG analysis. This provides a reasonable estimate of oil/plasticizer content if corrected for various low molecular polymeric and nonpolymeric (excess curatives, antioxidant fragments, etc.) material removed with the oil. However, composition of the vulcanizate is altered by extraction, and the lengthy extraction procedure is time consuming. The method therefore offers little advantage over the classical chemical method.

2. Establish a "correction curve" based on a reference temperature for a given polymer compound. This procedure is somewhat lengthy and requires knowledge of the polymer and oil types as well as the curatives.

3. Analyze isothermally below the polymer decomposition temperature.

4. Use reduced pressure to aid in removing oil at a lower temperature where polymer decomposition is not significant.

Both methods 3 and 4 have attracted renewed interest recently and will be discussed next.

Zeyen[25] advocated isothermal TG to estimate oil and plasticizer. He recommended dynamic TG to identify the temperature ranges and then to run isothermal TG at selected temperatures within the range to establish a "critical temperature" that permits the volatilization of the oil/plasticizer but does not volatilize the elastomer. Figure 10 illustrates the use of the isothermal TG on a rubber compound to confirm that the "critical temperature" has been correctly defined. Note that the sample is held at a constant temperature until the mass loss curve becomes constant. Zeyen observes that the analytical data for oil/plasticizer obtained by the isothermal method are a much better match to the known values than those determined by ASTM extraction method (ASTM D-297). The method works well for aromatic and napthenic oils. Paraffinic oils, used primarily in molded rubber goods (particularly in EPDM compounds), still covolatilize along with a portion of the polymer.

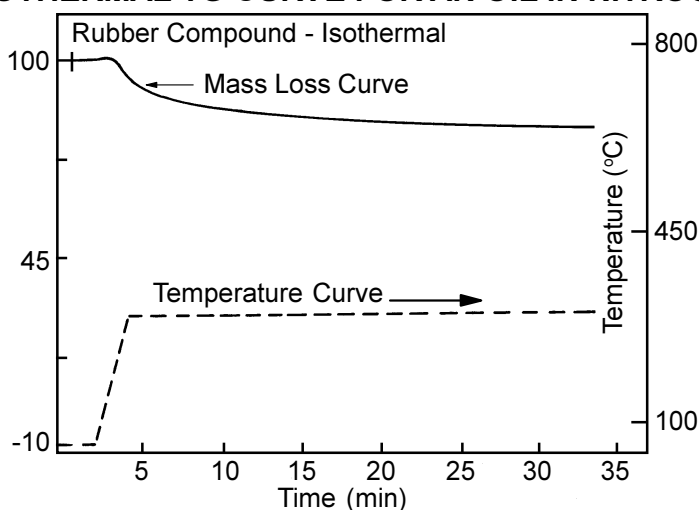### ISOTHERMAL TG CURVE FOR AN OIL IN NITROGEN

Figure 10

Another suggested solution is to use reduced pressure to alter the volatilization temperature of the oil and separate it from the polymer. Figure 11, scan A shows the effect of running the polymer alone in a nitrogen atmosphere versus running it under a vacuum of 0.5 mm of mercury[31]. Scan B shows a similar curve for process oil alone. The reduced pressure has a greater effect on the oil than on the polymer. This is clearly shown in scan C; the weight loss steps of 25 percent oil plus polymer are not resolved in nitrogen but are resolved at reduced pressure. Scans D and E show two more examples of polymer/oil weight loss resolution under vacuum versus nitrogen. Scan F shows a three component mixture into which air is introduced after the polymer loss has been completed. The usefulness of TG in studying oil/polymer separation in vacuo was also mentioned by T. Elisabeth[32] in 1983.

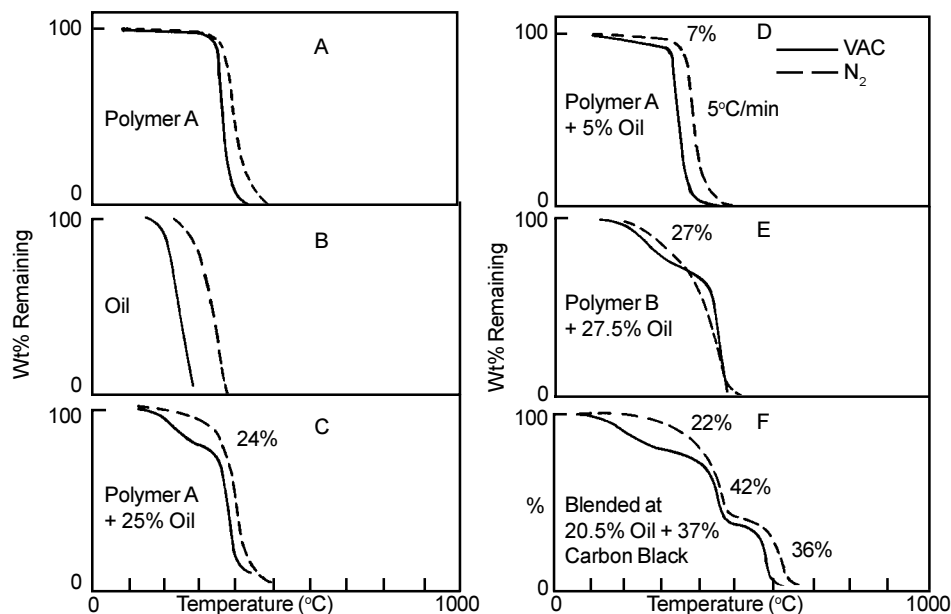### POLYMER/OIL WEIGHT LOSS RESOLUTION UNDER VACUUM VS NITROGEN

Figure 11

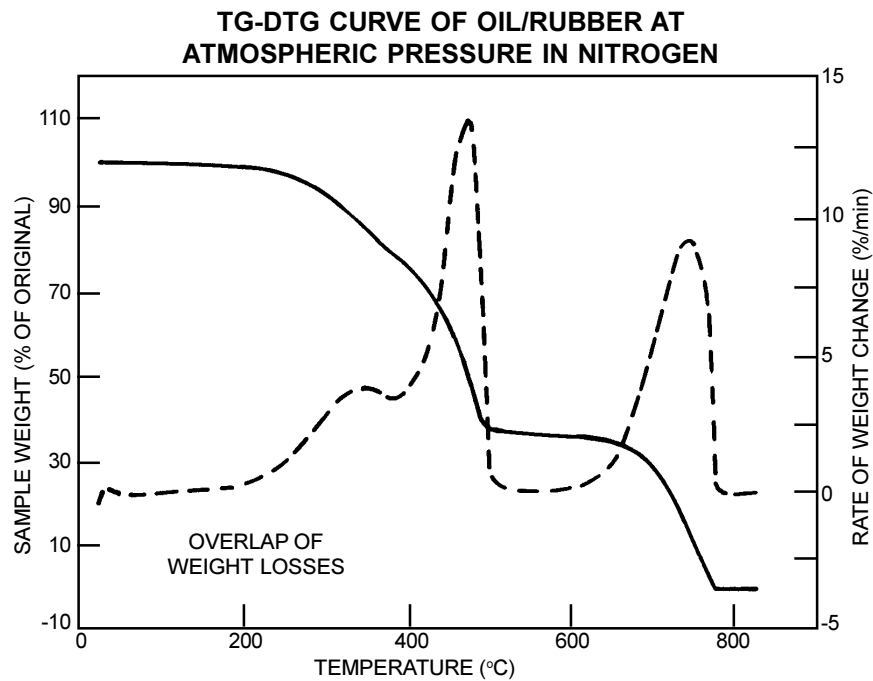## TG-DTG CURVE OF OIL/RUBBER AT ATMOSPHERIC PRESSURE IN NITROGEN

Figure 12

The method was further refined by Groves and Thomas[33] who combined isothermal TG with the vacuum technique. This is illustrated in Figures 12 through 14 for an unknown sample. TG-DTG in nitrogen indicates covolatilization of oil and rubber (Figure 12). Separation is slightly better in vacuum (Figure 13). Figure 14, where the vacuum and isothermal techniques were combined, shows complete separation of the oil and elastomer. The small dip in the TG curve is due to vacuum release. Incidentally, one of the TG manufacturers[34] recently announced a "High Resolution Thermogravimetric Analyzer" which, it claims, automatically senses the need and provides for an isothermal period, thereby eliminating the need for a preliminary dynamic TG run to locate the temperature range. The general concept of varying heating rate during TG weight changes is not new. The literature contains several references[35-38] which clearly illustrate that adjusting (slowing) the heating rate during weight changes improves resolution. However, in contrast to automatic sensing, these methods lengthen the experimental time substantially. Data are now being generated at the author's laboratory to explore the potential of this new method to provide better resolution of oil/plasticizer and elastomer curves.
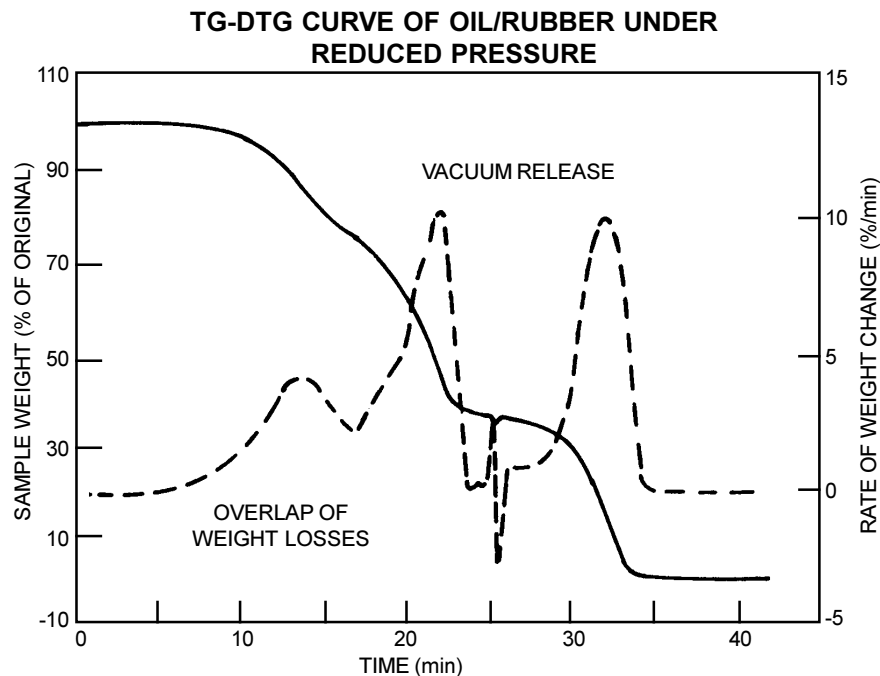
TG-DTG CURVE OF OIL/RUBBER UNDER REDUCED PRESSURE

Figure 13

TG-DTG CURVE OF OIL/RUBBER UNDER ISOTHERMAL AND REDUCED PRESSURE SHOWING COMPLETE SEPARATION OF OIL FROM RUBBER
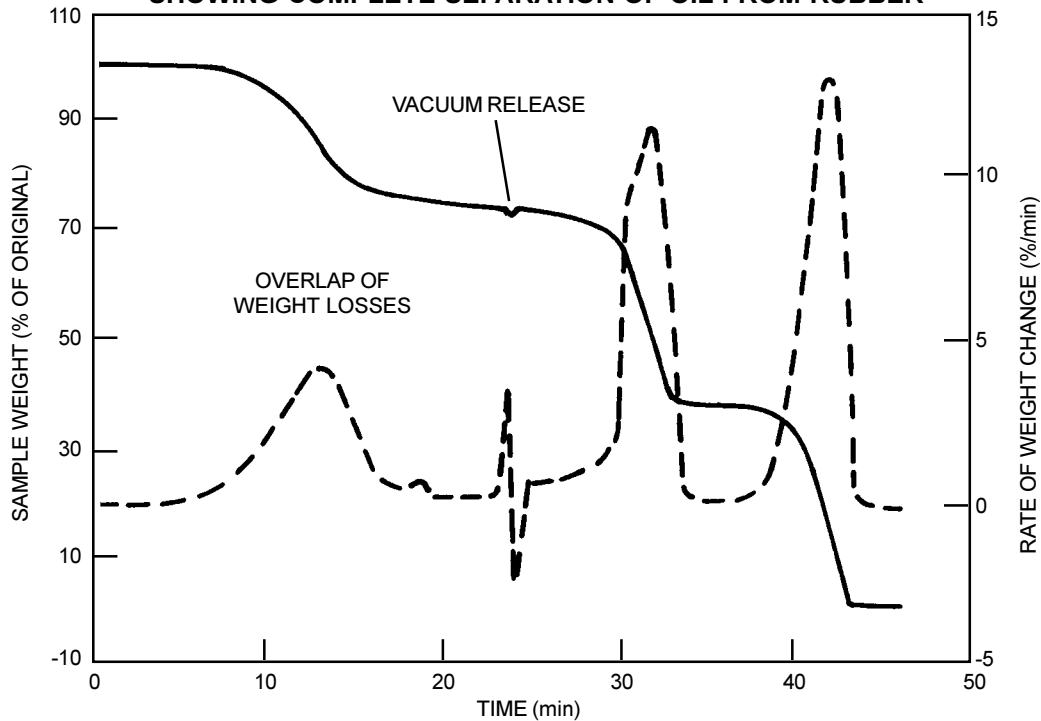

Figure 14

Determination of Polymer and Carbon Black in Elastomers with a Heteroatom

As mentioned before, the second and by far the greatest complication in compositional analysis of elastomer recipes by TG-DTG procedures is observed for polymers with a heteroatom in the constituent monomer. These polymers leave a carbonaceous residue (char) after degradation in nitrogen which is oxidized along with the carbon black included in the recipe when the environment is changed to air or oxygen. This gives a higher estimation of carbon black and a lower value of polymer than are actually present.

Table III shows the amount of carbonaceous residues obtained by pyrolyzing elastomers with different heteroatoms[17,39]. Similar data for chlorinated elastomers are shown in Table IV.[40] Data for NBR copolymers[19] will be presented later. It may be observed from Tables III and IV that carbonaceous residues estimated by different workers from the sample polymers are somewhat different. This is attributed to the following factors: 1) different chlorine content of different Poly (chloroprene) rubbers[41], 2) temperature of determination, 3) after treatment, (e.g., prolonged heating) and 4) rate of heating[42]. The amount of carbon residue depends on the polymer structure as well as the amount of chlorine in the polymer, and increases with the chlorine content in the same class of polymer. From a study of the degradation of chlorine containing polymers by TG, Jaroszyn' ska et al.[40] suggested that the quantity of nonvolatile carbon residue depends to a higher degree on the structure and ratio of the number of hydrogen atoms to chlorine atoms than on the chlorine content of the polymer. As may be observed in Table IV, PVC has the highest percentage of chlorine but leaves a substantially lower percentage of carbon residue than either chloroprene rubbers or Hydrin 100 after degradation. The literature data indicate that the chloroprene rubbers and the NBR copolymers, two commercially important elastomer categories, produce more char than the other elastomers studied and this introduces more error in the compositional analysis by TG. Therefore, our discussion shall be confined to TG-DTG analyses of these two elastomer categories in the rest of this review.

TABLE III

DTG CHARACTERISTICS AND CARBONACEOUS RESIDUES FOR MISCELLANEOUS ELASTOMERS

TYPE	ELASTOMER	% CARBONACEOUS RESIDUE (550°C) [17,39]
CR	NEOPRENE W	21.0
	NEOPRENE GT	22.0
	NEOPRENE AJ	23.0
CSM	HYPALON 20	2.0
	HYPALON 40	3.5
	HYPALON 45	2.0
FKM	VITON A	4.0
	VITON C-10	7.0
	VITON E-60	3.7
	VITON E-60C	4.0
	FLUOREL 2140	5.5
	FLUOREL 2160	8.0
CO	HYDRIN 100	13.0
ECO	HYDRIN 200	8.0
ACM	HYCAR 4041	7.5
	HYCAR 4042	6.0
	HYCAR 4043	5.0

TABLE IV

CARBON RESIDUES AFTER THERMAL DEGRADATION OF POLYMERS AT 550°C HEATED AT A RATE OF 20°C/MIN. IN NITROGEN ATMOSPHERE[40]

Type of polymer	Amount of chlorine weight, %	Carbon Residue weight, %
Poly(chloroprene) Rubber:		
Skyprene B-30	33.7	20.1
Neoprene WRT	37.2	24.6
Butachlor MC-10	34.2	22.5
Epichlorohydrine Polymers:		
Hydrin 100	35.6	11.1
Hydrin 200	24.0	7.5
Hydrin 400	23.7	6.5
Chlorinated Poly(ethylene)	42.0	6.5
Chlorosulfonated Poly(ethylene):		
Hypalon 20	28.5	3.6
Hypalon 40	33.0	4.5
PVC	52.0	8.5

Chloroprene rubbers. - A method was suggested[43] to determine the percent composition of chloroprene rubber in the recipe based on the amount of chlorine determined by the "Parr Peroxide Bomb" method[44]. A correction can then be made for the amount of carbon residue from the predetermined values of polymer char as in Tables III and IV. Table V summarizes the typical chlorine content of several chloroprene rubbers, as reported by the manufacturer,[45] versus those determined by the above method. The latter is somewhat lower but comparable to those reported by Jaroszyn'ska et al. (Table IV). Pure chloroprene rubber should contain 39.7 percent chlorine. However, the commercial chloroprene rubbers contain the added resin for emulsification, minuscule amounts of stabilizer, talc, water and occasionally sulfur as a comonomer. Since it is difficult to determine the type of chloroprene rubber polymer in a vulcanizate, an average value of 35.5 percent was used in the above work to indicate 100% chloroprene rubber.

TABLE V

PERCENT CHLORINE IN DIFFERENT NEOPRENES[43]

NEOPRENE TYPE	CO-MONOMER[+45]	%CL (TYPICAL)	%CL (ESTIMATED)
W	NONE	37.5	34.76
GW	Sulfur	39.8	36.20
GRT	Sulfur, 2,3-dichloro-1,3-butadiene	38.4	35.92
GNA	Sulfur	39.7	35.56
WHV	None	37.0	35.00
WRT	2,3-dichloro-1,3-butadiene	-	35.70

The TG curve for peroxide cured Neoprene W is shown in Figure 15. This indicates at least a three-stage degradation process for chloroprene rubber[46,47]. Brazier et al.[48] observed that carbon residue continues to decrease, at least up to 1000°C, although the loss is negligible after 550°C. The carbon residue values recorded in the literature are generally at 550°C and are therefore subject to a small error[17,39,40,43].
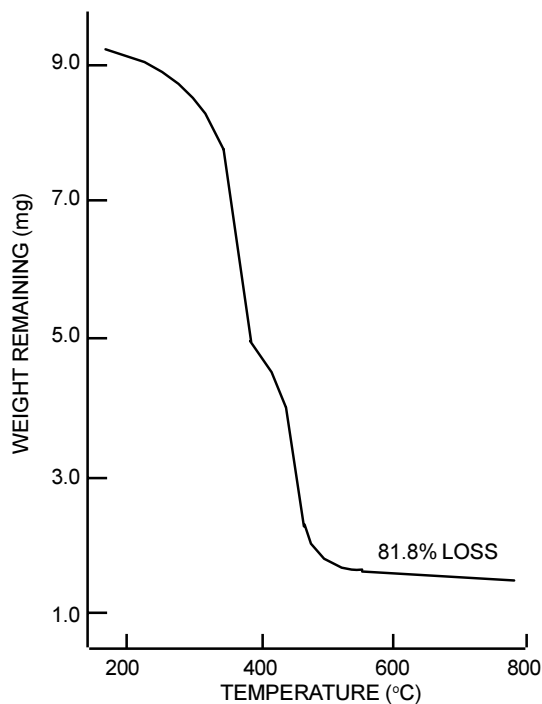
TG CURVE OF PEROXIDE CURED CR (9.19 mg)[46]

Figure 15

Carbon residue values of chloroprene rubber formulations containing different curatives are presented in Table VI. Raw Neoprene GRT (A_1) leaves substantially higher residue than WHV (A_2). This cannot be explained by their small difference in chlorine (Table V). It must be attributed to the presence of comonomers and sulfur in Neoprene GRT. The presence of ethylene thiourea accelerator alone (Sample B) does not seem to have any effect. Sulfur (Sample C) increases the residue, thus corroborating the suggested explanation for a higher carbon residue for GRT. Metallic oxides (Samples D and E), particularly zinc oxide, increase the residue. This is shown in TG and DTG curves of Figures 16 and 17 respectively. Figure 17 indicates that, in additional to an increase in the carbon residue, there are some changes in the mechanism of the reaction by progressive inclusion of metallic oxides and the curative. Decomposition is more rapid and occurs at a lower temperature by adding zinc oxide to Neoprene WHV. Further addition of magnesium oxide and ethynyl thiourea raises the peak temperature (first peak) by about 60°C, overlapping the second peak obtained with zinc oxide only (curve B). Inclusion of carbon black and some aromatic oil has a small additional effect on carbon residue as shown for Neoprene GNA in Table VII.
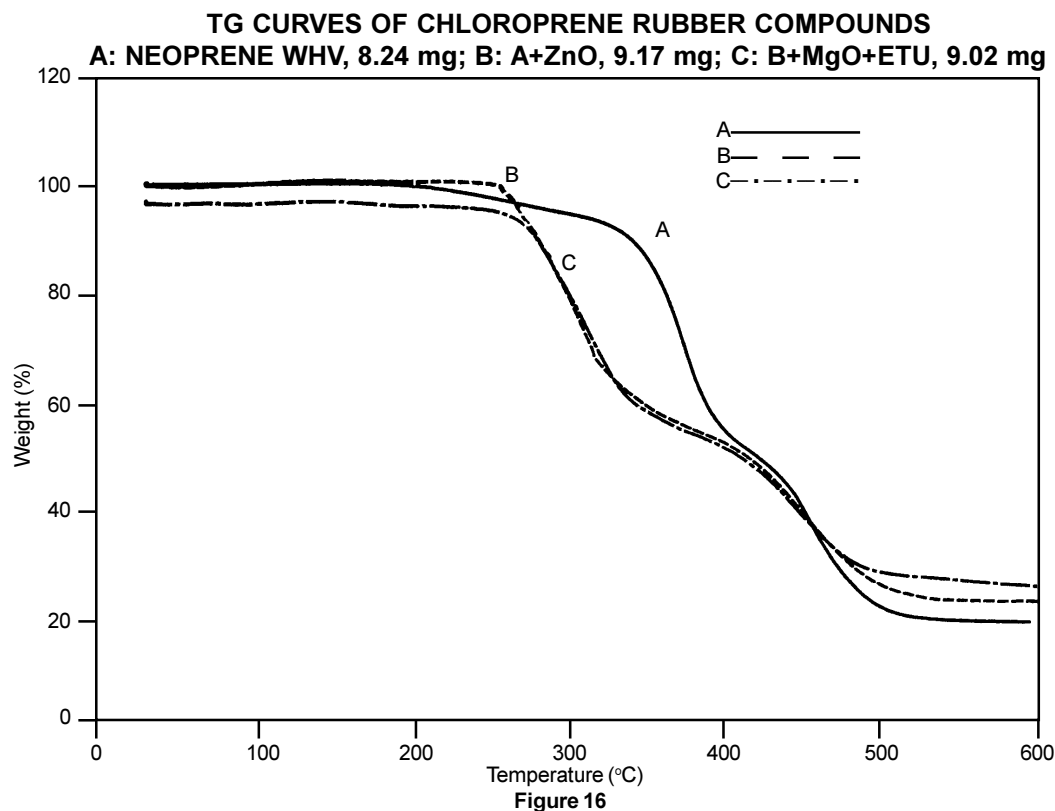
TABLE VI

THERMAL ANALYSIS OF CR RECIPES WITH CURATIVES[43]

RECIPES	A_1	A_2	B	C	D	E	F	G	H	I
CR,GRT	100	-	-	-	-	-	-	-	-	100
CR, WHV	-	100	100	100	100	100	100	100	100	-
ETU*	-	-	3	-	-	-	-	2	2	2
Sulfur	-	-	-	3	-	-	-	-	2	2
Magnesium Oxide	-	-	-	-	4	-	4	4	4	4
Zinc Oxide	-	-	-	-	-	5	5	5	5	5
DSC, T_p**	370	370	320	330	360	280	322	330	315	320
DTG, T_p***	368	370	370	374	355	260	315	320	320	325
CARBON, %	28.7	24.0	24.0	29.8	30.3	35.7	41.0	44.0	42.5	42.0

*Ethylene thiourea
**DSC Peak Temperature in °C
***DTG Peak Temperature in °C
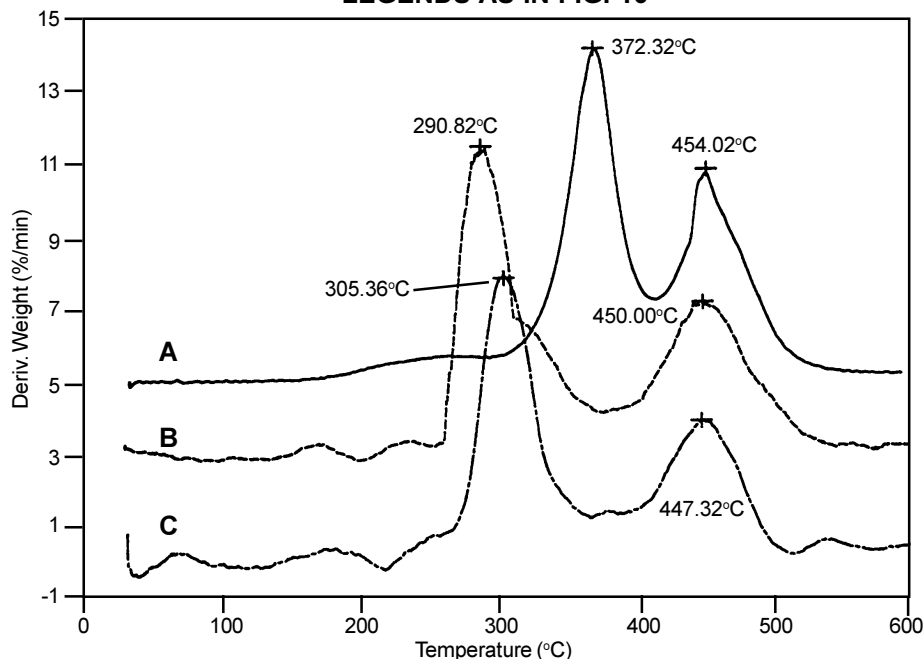

TG CURVES OF CHLOROPRENE RUBBER COMPOUNDS
A: NEOPRENE WHV, 8.24 mg; B: A+ZnO, 9.17 mg; C: B+MgO+ETU, 9.02 mg

Figure 16

DTG CURVES OF CHLOROPRENE RUBBER COMPOUNDS, LEGENDS AS IN FIG. 16

Figure 17

TABLE VII

COMPOUNDS VARYING IN CARBON BLACK AND OIL LOADING

	A	B	C	D	E	F
Neoprene GNA	100	100	100	100	100	100
Carbon Black, N650	23	30	37	-	-	-
Carbon Black, N351				23	30	20
*Hysil 233	-	-	-	-	-	10
**Agerite Resin D	2	2	2	2	2	2
Oil, Type 102 (Aromatic)	-	-	-	-	5	10
Magnesium Oxide	4	4	4	4	4	4
Zinc Oxide	5	5	5	5	5	5
TOTAL	134	141	148	134	146	151
% Carbon Black	17.2	21.3	25	17.2	20.6	13.2
% Carbon Char	38.3	39.8	40.1	38.6	41.7	39.7

*Precipitated hydrated silica
**Polymerized 1,2-dihydro-2,2,4 trimethylquinoline

It appears from the above discussion that accurate blank correction for the carbon residue of chloroprene rubber formulations would require rather comprehensive knowledge not only of the type of chloroprene rubber but also of the curative systems and carbon black loading, making it quite impractical for unknown vulcanizate analysis.

Acrylonitrile-butadiene rubber - Similar to the work mentioned above for chloroprene rubber, attempts were made to use a blank correction for NBR formulations, based on calibration curves, correlating carbon residue with acrylonitrile content of different NBR types[16,19,49]. Pautrat et al.[49] used nitrogen content of gum and loaded compounds for this purpose. Sircar and Lamond[16,19] also proposed a similar method which is described below.

The method proposes to identify different NBR types by their glass transition temperature (Tg, Figure 18). Figure 19 shows that the amount of carbon residue increases with the acrylonitrile content of NBR. A calibration curve of percent residue versus acrylonitrile content of NBR (Figure 20) then allows correction for the actual polymer and carbon black content.

VARIATION OF GLASS TRANSITION TEMPERATURE
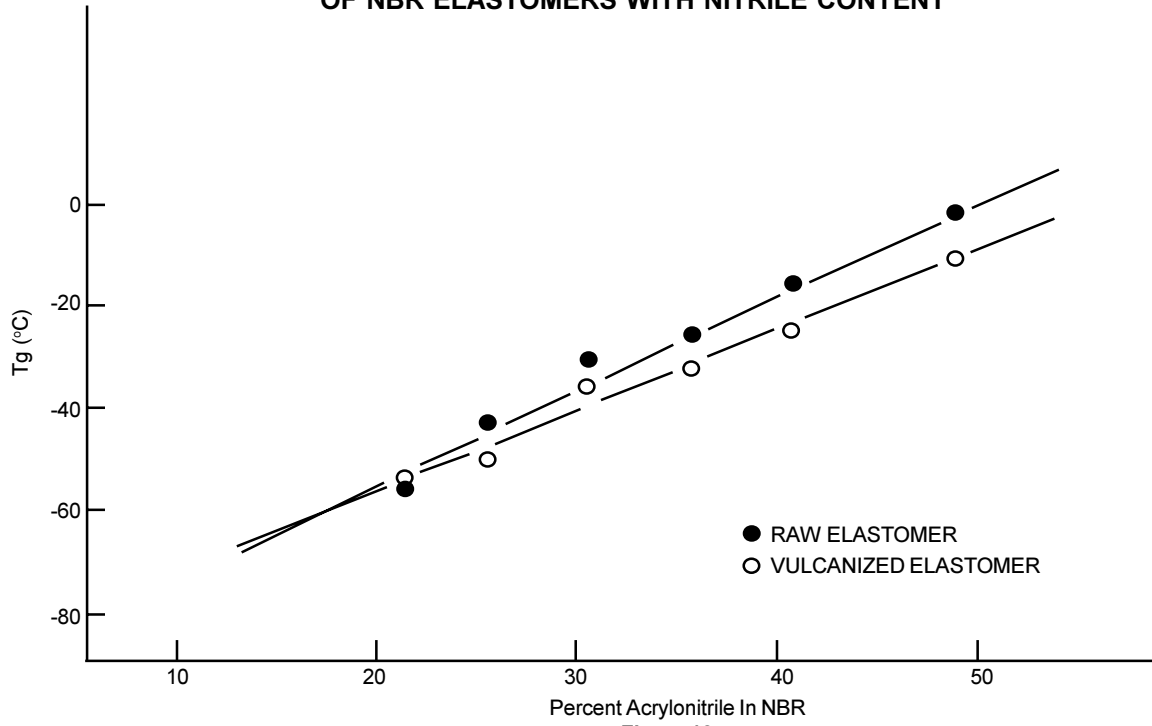## OF NBR ELASTOMERS WITH NITRILE CONTENT

● RAW ELASTOMER
○ VULCANIZED ELASTOMER

Percent Acrylonitrile In NBR

Figure 18

TG CURVES OF NBR RUBBERS IN NITROGEN

PAN

NBR 50%

NBR 25%

Temperature (°C)

Figure 19

VARIATION OF CARBON RESIDUE IN NITROGEN
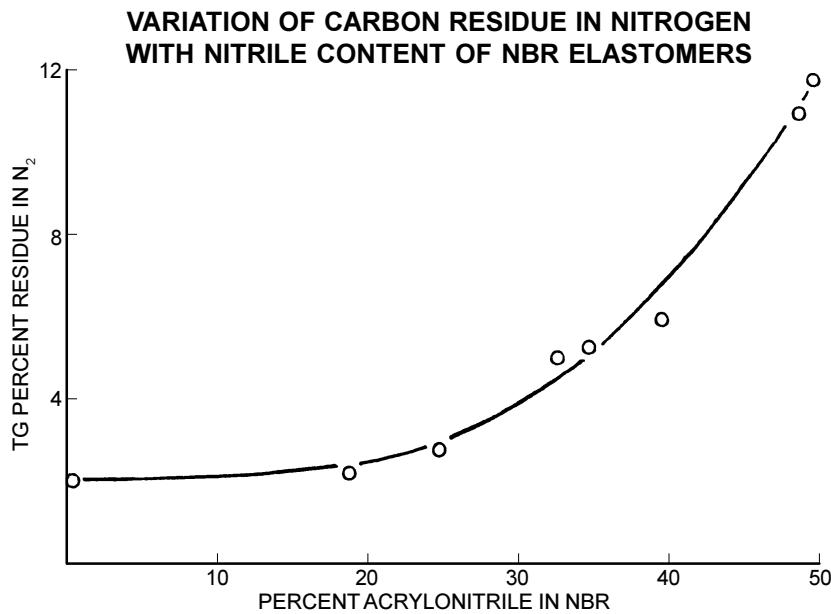## WITH NITRILE CONTENT OF NBR ELASTOMERS
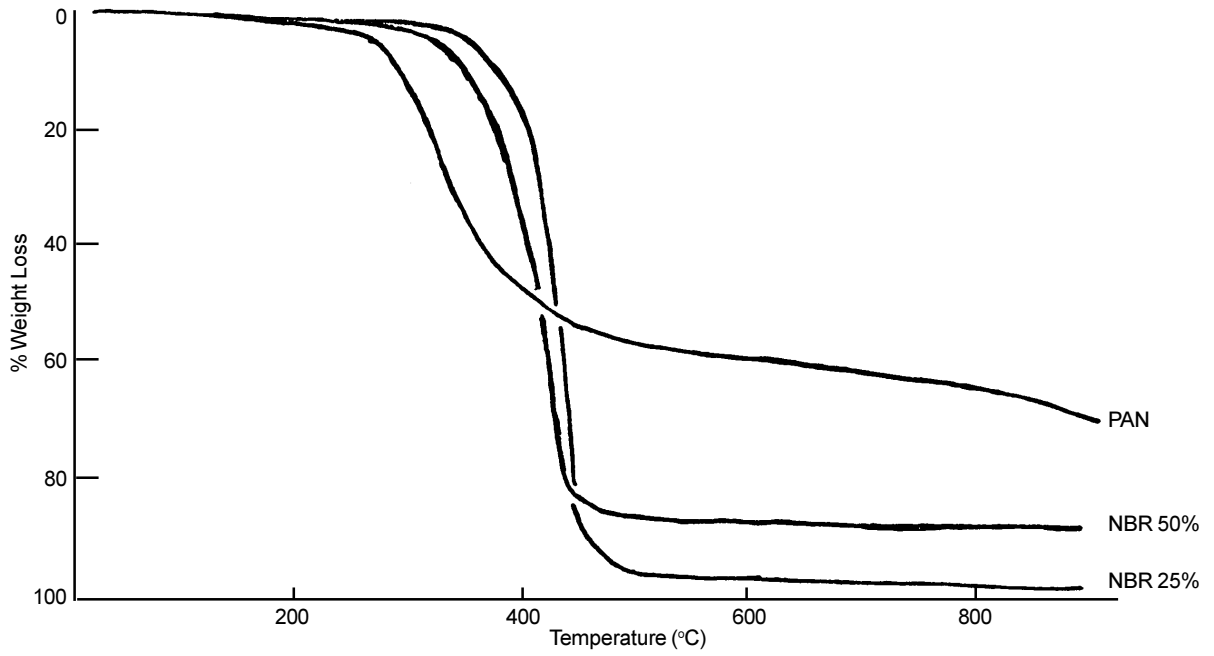
Figure 20

Although acceptable estimates (within 2 percent) of NBR vulcanizates were reported[16,19,49], more recent work indicates that the amount of carbon residue is a function of both the nitrile content of the rubber and the rubber content of the vulcanizate, making it rather difficult to analyze unknown vulcanizates. The residue is also affected by heating rate.

Swarin and Wims[7] described the successful analysis of an O-ring formulation based on NBR which contained N550 black and graphite. These authors observed three separate peaks in TG-DTG curves for their NBR formulations with peak temperatures around 475°C, 575°C and 760°C, ascribed to the oxidation of polymer residue, carbon black and graphite respectively (Figure 21). The derivative signal was used to establish the differences between the weight loss steps and thus determine the percentages of polymer, carbon black, and graphite. The medium particle size black used oxidizes at a higher temperature and this allows the separate estimate of polymer residue and carbon black. Other work[47,50] with smaller particle size blacks (HAF, EPC, and SAF) reported difficulty in resolving the two DTG peaks. The relative oxidation characteristics of the carbon residue and the carbon black will influence the degree to which DTG will enable resolution of these events. To add to the complication, Schwartz and Brazier[48] observed that the same black, recovered after pyrolysis, is more reactive than the virgin black. Also the same grade produced at different locations by the same or different manufacturers have different oxidation rates. This may be attributed to the differences in soluble inorganic matter in quench water used for the production of the furnace blacks. Metallic oxides are known to catalyze oxidation of carbon blacks[51].
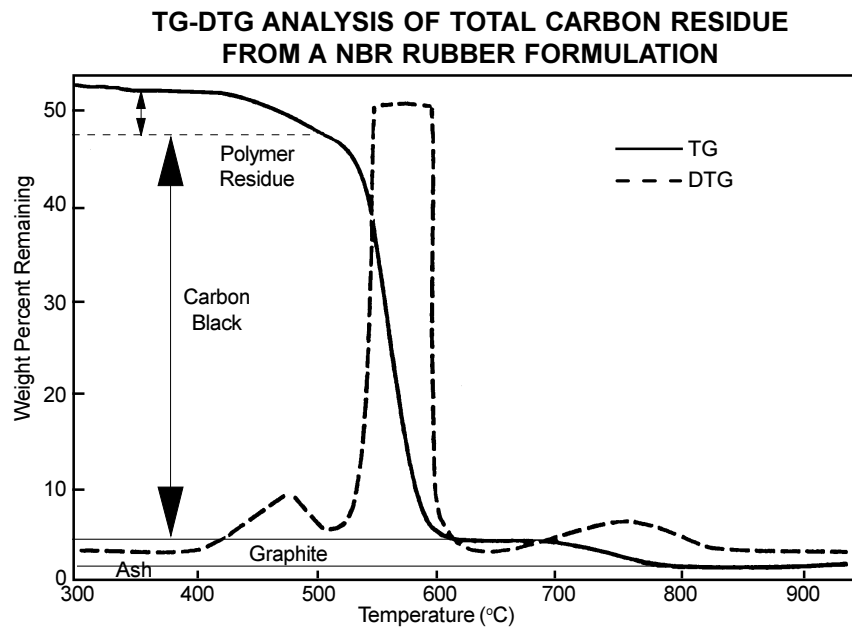
TG-DTG ANALYSIS OF TOTAL CARBON RESIDUE
FROM A NBR RUBBER FORMULATION

Figure 21

**TG-DTG CURVES FOR THE OXIDATION OF CARBON RESIDUE FROM THE
PYROLYSIS IN NITROGEN ATMOSPHERE OF A NEOPRENE VULCANIZATE,
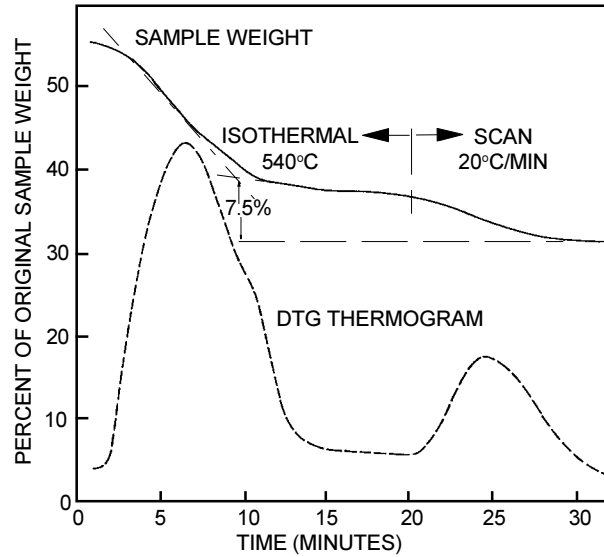CONTAINING 9% OF N550 BLACK AND 36.5% INORGANICS**

Figure 22

Schwartz and Brazier[48] used isothermal oxidation in an atmosphere of 7 percent oxygen to lower the oxidation rate of carbon blacks. Under these conditions, good estimates could be made for carbonaceous residue from Neoprene W and N550 black (Figure 22) and for a more complex system containing NR, and Neoprene WRT as well as a mixture of N990 and N326 blacks (Figure 23). Similar results could also be obtained with carbonizing NBR vulcanizates as illustrated in Figure 24. In agreement with earlier work by Pautrat et al.[49] who used dynamic TG, Schwartz and Brazier observed that fine particle size blacks (N110, N330 etc.) oxidize at the same temperature as the residue from NBR, where as the coarse blacks (N770, N990 etc) oxidize at a much higher temperature and can be separated from the NBR carbonaceous residue. By proper choice of an appropriate isothermal temperature and dilute oxygen atmosphere, the DTG oxidation peaks of medium particle size reinforcing blacks (N550, N660 etc.) can also be separated from that of the carbonaceous residue. However, as indicated above, not all char forming polymers can be estimated in this manner in presence of all carbon blacks. The nature and quantity of carbon residue may also be different depending on the type of NBR and the nature and amount of the curatives. To complicate matters, some aromatic oils also leave a small amount of carbon residue after volatilization. Graphite oxidizes at approximately 800°C (Figure 21) and can be determined in the absence of calcium carbonate which decomposes liberating carbon dioxide at about the same temperature. However, use of nitrogen atmosphere for calcium carbonate and subsequent oxygen atmosphere for graphite should enable analysis of both.

**TG-DTG CURVES FOR THE OXIDATION OF CARBON RESIDUE FROM THE
PYROLYSIS IN NITROGEN OF A 50:50 NR/NEOPRENE WRT BLEND
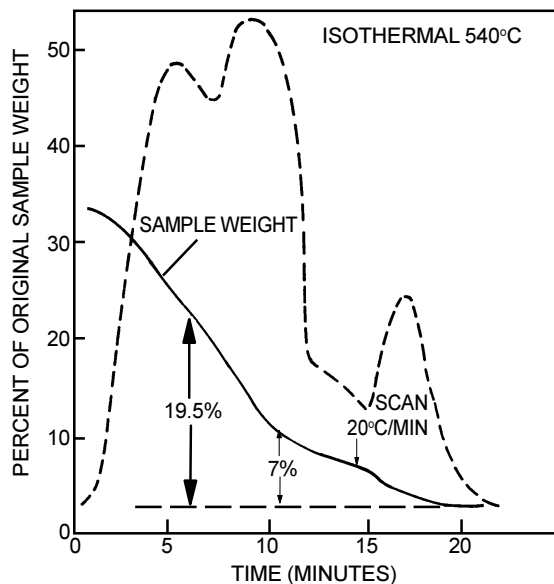CONTAINING 13.5% N326 AND 6.7% N990 CARBON BLACKS**

Figure 23

TG-DTG CURVES FOR THE OXIDATION OF CARBON RESIDUE FROM THE PYROLYSIS OF AN 85:15, 34% NBR/EPDM BLEND, CONTAINING 30% N326 BLACK
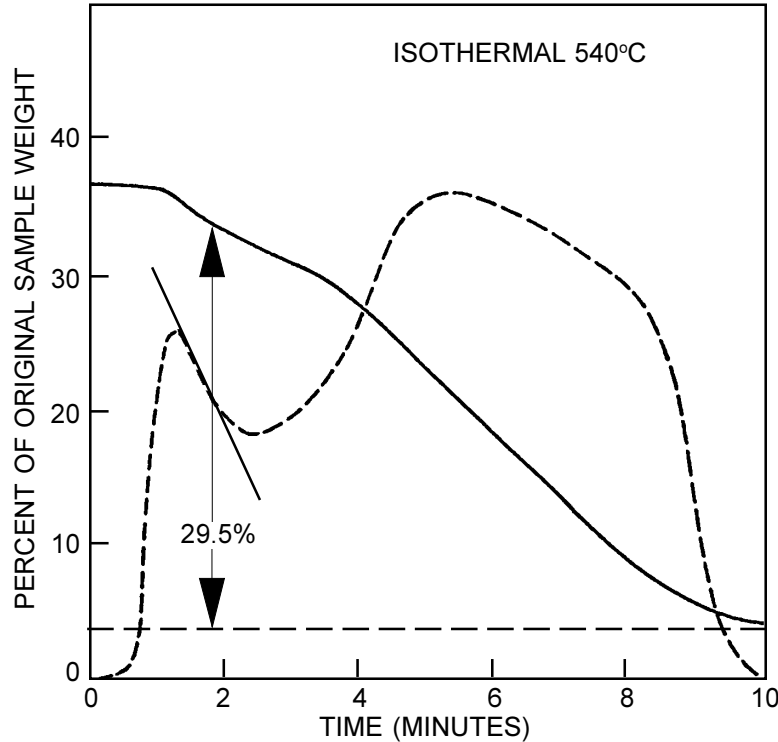

Figure 24

CONCLUSIONS

The overlap in the TG-DTG curves for oil/plasticizer and elastomer may be minimized or eliminated by carrying out the experiment under vacuum and/or an isothermal temperature predetermined by a separate dynamic TG-DTG experiment or by an improved sensing device. However, more work needs to be done with different oil, plasticizer, resin, curatives, and elastomer combinations to identify their different characteristics and to draw conclusions with justifiable confidence.

The most promising approach to resolving the issue of separating polymer char and carbon black oxidation peaks in TG-DTG experiments lies in the use of lean oxygen gas. Further work needs to be carried out with different lean gases (different nitrogen/oxygen or helium/oxygen ratios) to investigate their effects on different formulations which can not be analyzed at present with 7 percent oxygen. It is possible that different feed rates of lean gases would improve the resolution as was reported recently[52] for NBR formulations. It is conceivable that imposition of a lower rate of heating, an isothermal oxidation and/or vacuum, along with a slow feed of lean oxygen would help. It will be interesting to explore the "High Resolution Thermogravimetric Analyzer" to help resolve the TG-DTG curves. It may, however, be mentioned that the carbon residues from other heteroatom elastomers (Tables III and IV) are not as high as those from CR and high nitrile NBR. Therefore, the error caused by their inclusion as carbon black will be relatively small. This explains the lack of mention of carbon residue in the TG-DTG analysis of carbon-loaded low nitrile vulcanizate by some authors[53,54].

In conclusion, it may be mentioned that despite the difficulties mentioned above, TG-DTG analysis remains a powerful tool for the compositional analysis of vulcanizates. Because of its simplicity, reasonable accurate data for most vulcanizates, and economy of time over the classical method which requires extraction, it remains the method of choice for compositional analysis of vulcanizates wherever TG-DTG equipment is available.

ACKNOWLEDGMENT

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