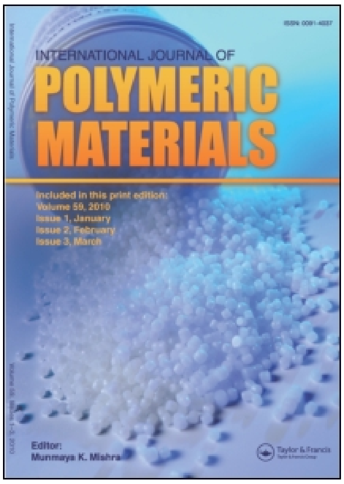

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Staicu, Doina , Stoica, Stela , Ciupitoiu, Alexandra and Topciu, Elena(1990) 'A Method for the Estimation of the Efficiency of Antioxidants in Secondary Polyolefines Stabilized According to the Defects Dilution Process', International Journal of Polymeric Materials, 14: 1, 53 — 65

To link to this Article: DOI: 10.1080/00914039008041071

URL: http://dx.doi.org/10.1080/00914039008041071

Intern. J. Polymeric Mater., 1990, Vol. 14, pp. 53–65
Reprints available directly from the publisher
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Printed in the United Kingdom

A Method for the Estimation of the Efficiency of Antioxidants in Secondary Polyolefines Stabilized According to the Defects Dilution Process

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The defects dilution principle was checked for secondary polypropylene from used electric accumulators. According to this principle, after a determined number of reprocessings, through modification with the same quantity of raw material, the active species resulted from ageing, uniformly distributed in the polymer mass, occur in such a quantity which determines a constant level of thermooxidative stability. The estimation of fenolic antioxidants efficiency from the difference between the melting point of regenerated polymer and his oxidation temperature, determined by using differential thermal analysis is an adequate method for secondary polypropylene from used electric accumulators, stabilized according to the defects dilution process.

KEYWORDS: Efficiency, antioxidants, method, polyolefines, stabilization, defects

1. INTRODUCTION

The degradation and stabilization of secondary polymers have particular characteristics different from those specific of raw polymers because of the chemical active species resulted through the ageing of polymer during his life and of the impossibility to completely eliminate the residual impurities content.

The opinions about secondary polymer stabilization differ, most of them being actually impossible.[1]

In equal measure, the idea of supplementary stabilization of raw material at processing is accepted, to ensure the additive for inhibiting the destructive active species.[2]

According to the dilution principle[3] the mentioned difficulties of secondary polymers stabilizations can be overpassed, because after 4,5 reprocessing, through modification with the same quantity of raw material, the fraction from

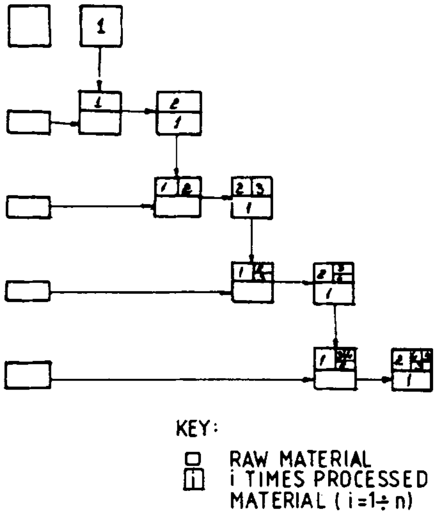

FIGURE 1 The effects dilution process when it is used a blend with 50% recovered material and 50% raw material.

the product unity supported the maximum number of reprocessings become negligible and uniformly distributed in the polymer mass (Figure 1). As a result of the defects dilution process, after a number of processing-using cycles, there is the possibility to reach a constant level of the product properties (Figure 2).

The practical importance of thermal analysis at linear heating rates for the study of the influence of additives on polymer degradation has been demonstrated.[4] Knowledge of the mechanism of oxidation reactions at higher temperatures is important for the technology of polymer processing, even though these processes occur in the presence of low concentrations of oxygen.

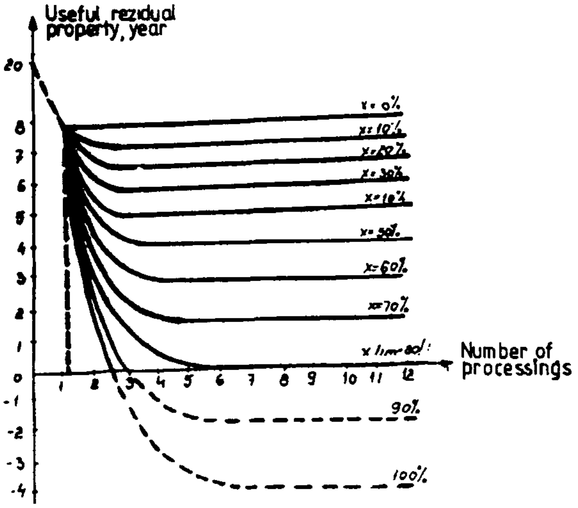

FIGURE 2 The constant level of useful residual property for various recovered material percents in blend with raw material.

Thermogravimetric analysis of stabilized polymeric system gives a more accurate assessment of the effects of stabilizer volatility on polymer degradation.[5]

The purpose of this essay is to verify the defect dilution process for degradation products appeared after thermooxidation, at constant impurities content, for secondary polypropylene from used electrical accumulators, using the thermogravimetric analysis for the estimation of the fenolic antioxidant stabilization efficiency.

2. EXPERIMENTAL

The secondary polypropylene, from used electrical accumulators, after washing (the residual impurities content 8%) and grinding, was regenerated, according to the dilution process of the defect, through modification with 50% raw material and thermooxidative aged, 3 h at 150 °C, even in air after each regeneration cycle (Figure 3).

The mixing of the secondary with raw polymer was made in a laboratory mixer, with 700 rot./min speed, during 5 min.

After granulation (200°C on nozzle), the regenerated polymer was injected (T nozzle: 200°C, *t* injection: 13 sec., pressure injection: 700 atm) in samples that were aged by thermooxidation.

Raw and secondary polymers were subjected to a similar reprocessing-ageing sequence, without being modified with raw material, both of them supporting only three cycles.

The value of regenerated (R), secondary (S) and raw (P) polymer degradation

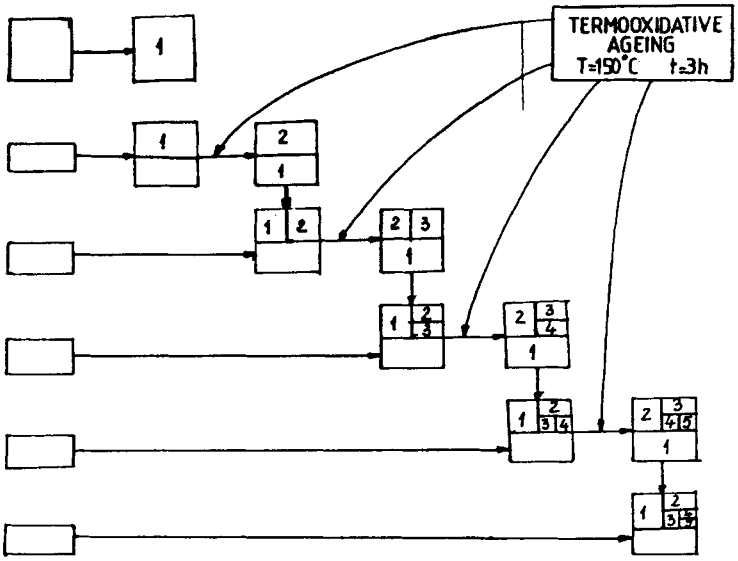

FIGURE 3 The regeneration process and artificial ageing condition.

was estimated through determination of the:

– molecular weights-viscozimetric measurements, in heptan at 60°C

– carbonyl groups-referring to the IR absorption from 1790 cm^{-1} at those from 1310 cm^{-1}. The IR spectra were registered red on a Perkin Elmer spectrophotometer, on 0.1 mm films, hot pressed, 5 min. at 198°C, at 11 atm. and cooled, 10 min. at 150 atm.

–thermooxidative stability-through Brabender ($T = 200°C$ speed = 60 rot/min..tank = 30 cm^3), oxygen absorbtion (at 170°C) and thermogravimetric (DTA: 50 V, TGA: 100 mm, at a heating rate of 6 min^{-1}, from ambient temperature to 500°C) methods.

The regenerated polymers resulted from the cycles that ensure a constant level of thermooxidative stability were stabilized with calcium stearat 0.1% at 100% polymer and different fenolic antioxidants (Hostanox O_3, Irganox 1010, 1076 and 1425) added to the same number of functional groups (0.125 10^{-3} g.f./mol). The inclusion of the stabilizers into polymer was made through mixing 7 min. at 200°C in a Brabender plastometer.

3. RESULTS AND DISCUSSIONS

The Table I shows that if the average molecular weight for raw and secondary polymer decreases with the growth of the reprocessing number, for regenerated polymer is roughly constant and equal with those calculated additive considering the average molecular weight of the constituents polymeric types (Table I)

The reprocessings is determined the growing of the carbonyl content for raw and secondary polymers and reaching a constant value, proper to the raw material for regenerated polymer (Figure 4).

The variation of the Brabender mixing torque, with the destruction time decreases for P and S samples series and growing till the comparable value of the raw polymer for R sample series (Figures 5–7)

The oxygen absorbtion method shows a decrease of the thermostability in P_{0-3} (Figure 8) and S_{1-4} (Figure 9) series and a growing for R samples (Figure 10)

The analysis of the variation of the thermostability of regenerated samples with the number of reprocessing determined through those methods shows the reaching of a constant level for thermostability after four cycles, similar in value with those of the polymer which was used for modification (Figures 11, 12).

The differential thermal analysis of the regenerated polymer that has a constant level of the thermostability (resulted after 4 and 5 reprocessings) shows that these have similar melting point (152°C). The temperature intervals in which occurs the oxygen uptakes reaction are the same (152–250°C). The degradation reaction with loss of mass begins at the same temperature (250°C), (Figure 13).

As we demonstrated before, it follows that, according to the defects dilution principle, the active species resulted from thermooxidative ageing are diluted with reprocessing, the constant level of the thermostability reached through regenera-

TABLE I

Variation of medium viscozimetry molecular weight for raw, secondary and regenerated polymer as a function of the number of processings

	Number of processings									
	0		1		2		3		4	
	Medium molecular weight									
Polymer	Viscozimetry test	Calculated	Viscozimetry test	Calculated	Viscozimetry test	Calculated	Viscozimetry test	Calculated	Viscozimetry test	Calculated
Raw	303,300	—	276,700	—	256,500	—	192,020	—	—	—
Secondary	225,870	—	213,700	—	198,150	—	194,260	—	—	—
Regenerated	260,200	263,585	263,500	252,887	261,532	277,700	254,400	277,029	273,050	264,889

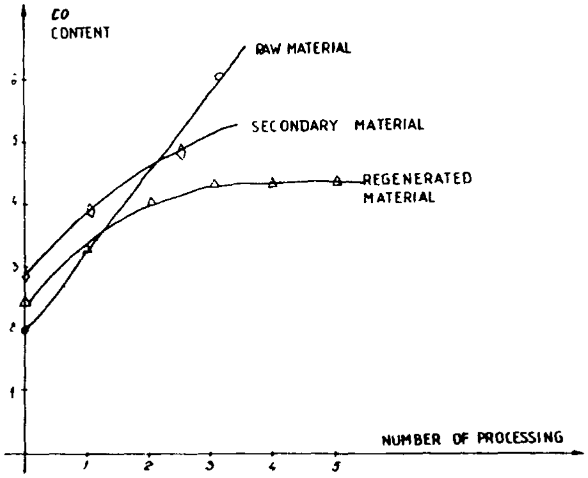

FIGURE 4 Variation of the CO content for raw secondary and regenerated polymer with the number of processing.

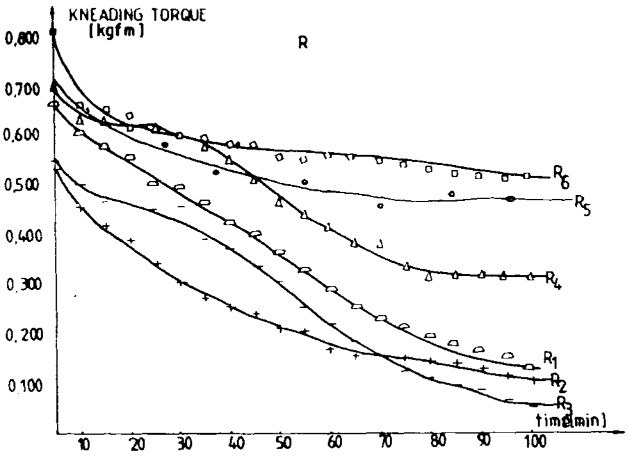

FIGURE 5 Variation of kneading torque for regenerated polymer as a function of time.

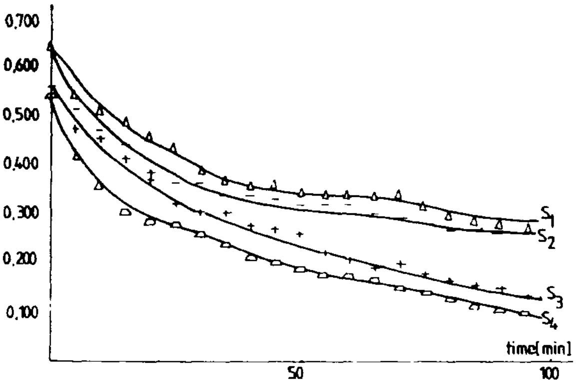

FIGURE 6 Variation of kneading torque for reprocessed secondary polymer as a function of time.

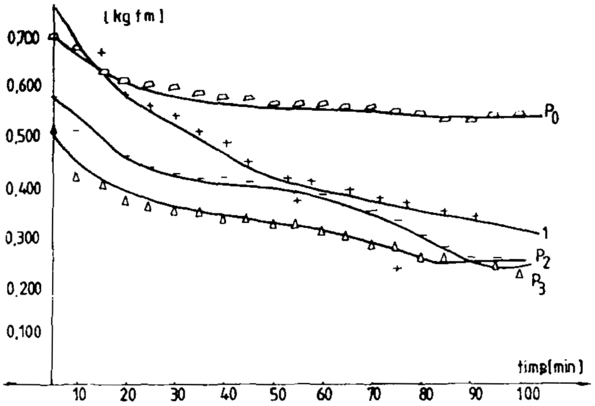

FIGURE 7 Variation of kneading torque for reprocessed raw polymer as a function of time.

tion, being a function of type of raw material, the modification percent and the nature of the ageing process.

Figures 14 and 15 compare the thermal degradation of regenerated polypropylene according to the defects dilution process with constant level of the thermooxidative stability with those of the same polymers thermooxidative stabilized with formulae in which different fenolic antioxidants were used.

All the cases show anendothermal peak at 162°C due to the melting of the polypropylene, there after, differences in behaviour are observed, the oxygen absorption reaction being delayed for polymers with antioxidants, with a temperature interval pending to the stabilizers efficiency.

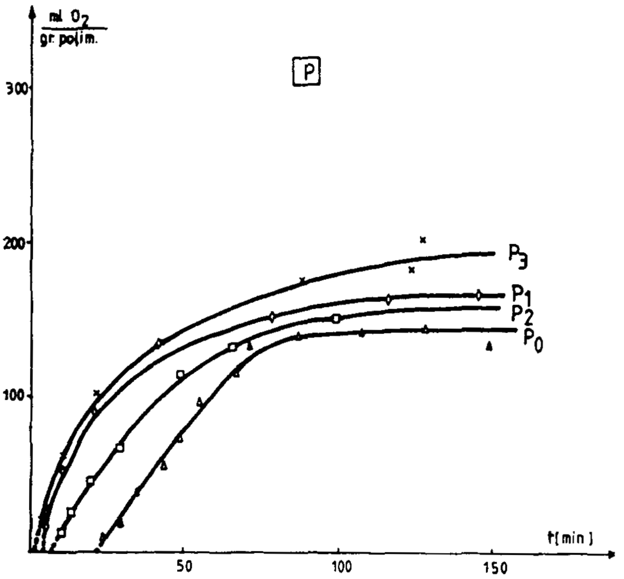

FIGURE 8 Variation of oxygen absorbtion for reprocessed raw polymer as a function of time.

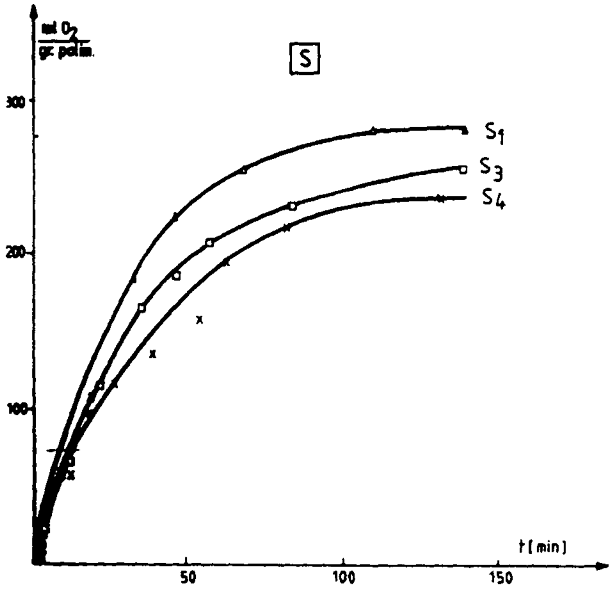

FIGURE 9 Variation of oxygen absorbtion for reprocessed secondary polymer as a function of time.

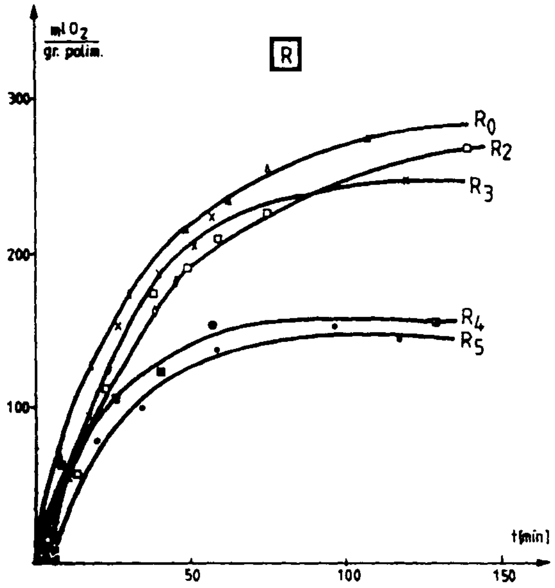

FIGURE 10 Variation of oxygen absorbtion for regenerate polymer as a function of time.

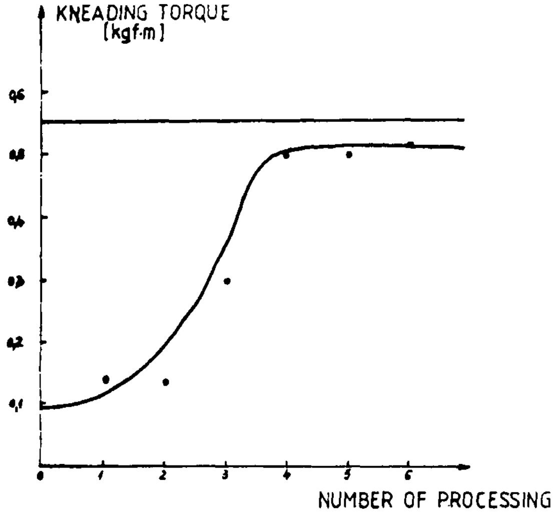

FIGURE 11 Variation of kneading torque after 100 min, for regenerated polymer as a function of the number of processing.

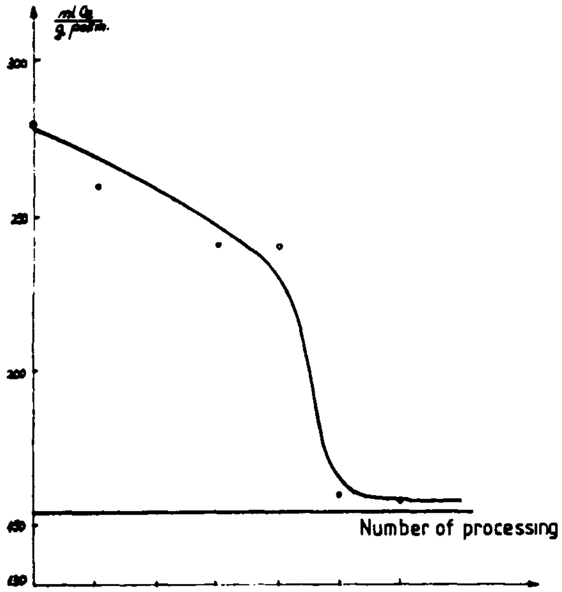

FIGURE 12 Variation of oxygen absorbtion for regenerated polymer, after 50 min. As a function of the number of processings.

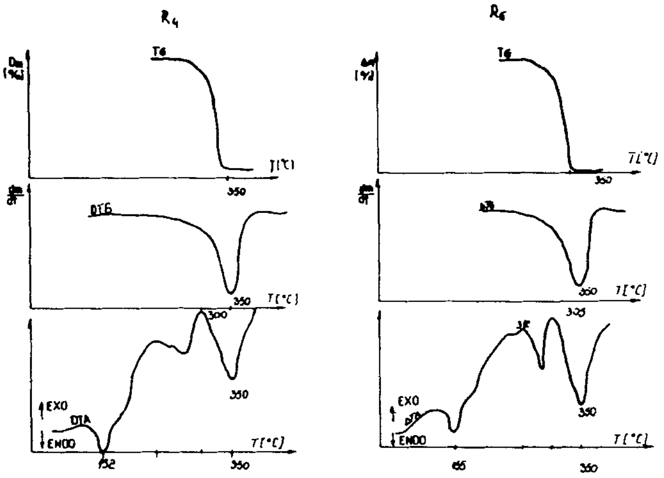

FIGURE 13 DTA, TG and DTG diagrams for regenerated polymers (R_{45}) which reached constant level of thermooxidative stability.

Because of the constant level of the thermooxidative stability reached through regenerations, the thermooxidative behaviour of the two polymers, R_4 and R_5, is similar and the conclusions about the efficiency of stabilizers are the same.

4. CONCLUSIONS

1. The defects dilution principle, according to which after a determined number of reprocessing through modifications with the same quantity of raw material, the active species resulted from ageing, uniformly distributed in the polymer mass, there are in such a quantity that determines a constant level of thermooxidative stability, was checked for secondary popypropylene from used electric accumulators.
2. The estimation of the fenolic antioxidants efficiency from the difference between the melting point of regenerated polymer and his oxidation temperature, determined using differential thermal analysis is an adequate method for secondary polypropylene from used electric accumulators, stabilized according to the defects dilution process.
3. It is necessary to verify these conclusions for the case of the influence of the deluted impurities of the secondary polymer on the level of thermal stability of the regenerated polymer.

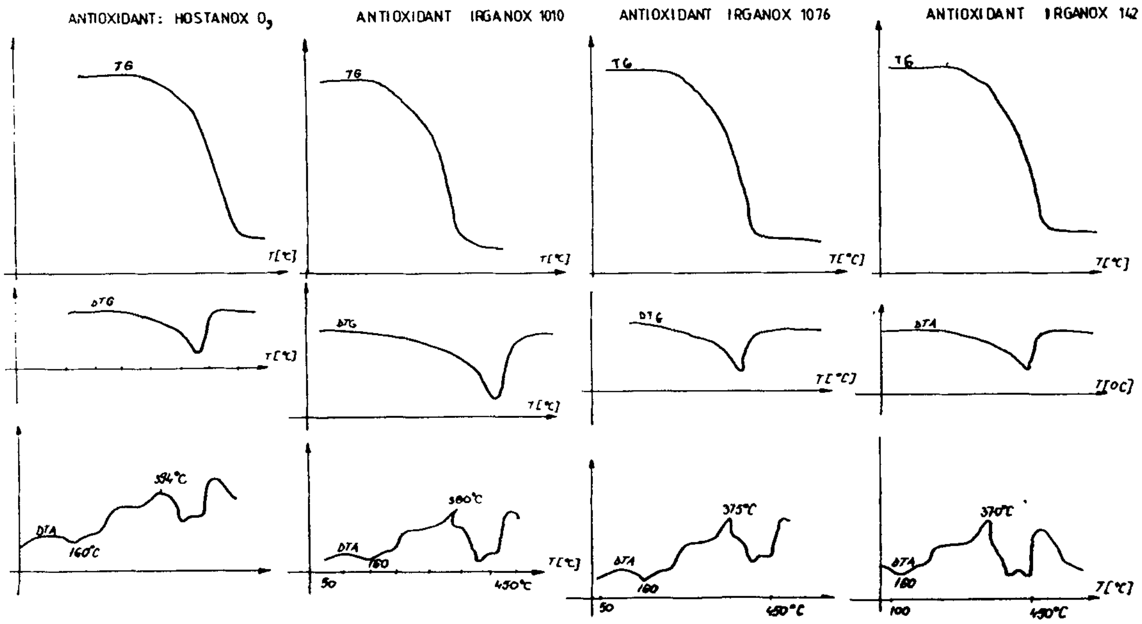

FIGURE 14 DTA, TG and DTG diagrams for regenerated polymer-R_4-stabilized with different fenolic antioxidants.

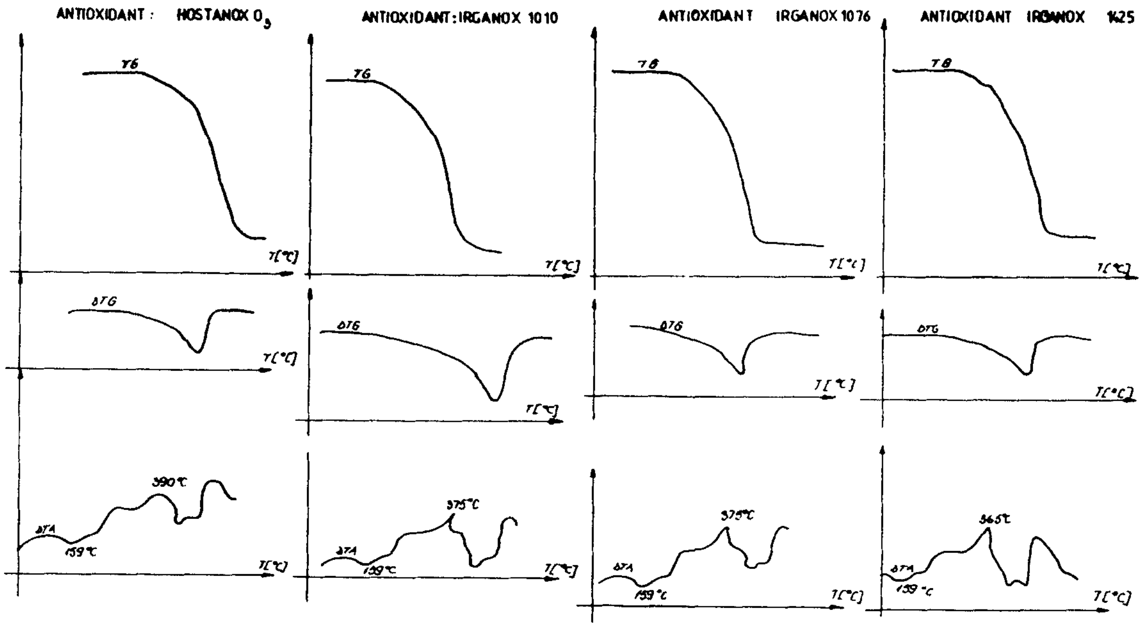

FIGURE 15 DTG TG diagrams for regenerated polymer-R_5-stabilized with different fenolic antioxidants.

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