

The Early Stages of Isotactic Polypropylene Oxidation*

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INTRODUCTION

The oxidative degradation of polypropylene presents a more serious problem than that of polyethylene. Many antioxidants, such as 4,4'-thiobis(3-methyl-6-*tert*-butylphenol), which give excellent protection to polyethylene at concentrations of 0.1% or less, are either ineffective when used in polypropylene or must be present in concentrations of over 0.5% to provide any significant degree of protection.

The oxygen absorption of polypropylenes at various temperatures¹ gives curves similar to those obtained with polyethylenes. The induction periods, however, are considerably shorter and the autocatalytic rates are more rapid. In the case of polyethylene, Hawkins et al.² have shown that when about 0.5% of oxygen (corresponding to about 3.5 ml. of oxygen per gram of polymer) had been absorbed, the mechanical and electrical properties were degraded to such an extent that the polymer was no longer suitable for wire and cable insulation. Similar studies of polypropylene have not yet been reported. It was therefore highly desirable to study the initial stages (up to where about 10 ml. of oxygen per gram of polymer is consumed) of the thermal oxidation of a typical isotactic polypropylene, to determine the effects upon electrical properties and at the same time gain some understanding of the factors involved.

Since it has been our experience that differently based polypropylenes show different susceptibilities to oxidation, it was decided to carry out the entire study with one sample of polymer.

EXPERIMENTAL

The polypropylene used was an unstabilized powder having a melt index of 3.0. Heptane extraction³ left a residue of 92.0%. Infrared examination of 10 ml. sheets showed the presence of a small amount of carbonyl groups, equivalent to less than 0.1 ml. of oxygen per gram of polymer. The ash content was 0.05%. The sample was stored under nitrogen. The test sheets were compression-molded directly from the powdered poly-

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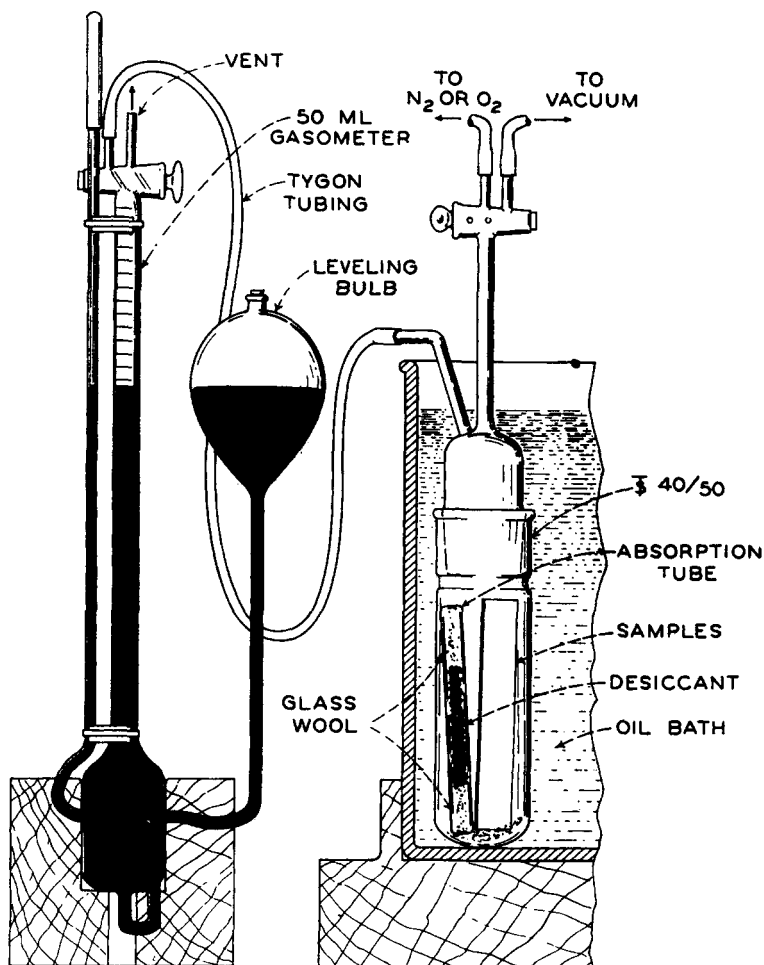


Fig. 1. Apparatus for oxidation studies.

mer by means of "picture frame molds" of the desired thickness and aluminum parting sheets. The total molding time required was about 3 min.

The oxidations were carried out at $130^{\circ} \pm 0.5^{\circ}\text{C}$. in the apparatus shown in Figure 1. The samples were placed in the 2×8 in. glass reactor immersed in a silicone oil bath. An absorption tube filled with Linde No. 5A molecular sieves for absorbing volatile products was also placed in the reactor. The oxygen consumption was measured with a 50 ml. gas buret. A stopcock at the top of the reactor permitted evacuation and filling with either nitrogen or oxygen. To obtain an accurate starting time, t_0 , the reactor was kept filled with nitrogen until thermal equilibrium had been established. It was then evacuated and filled with oxygen.

When it was necessary to oxidize the polymer to a given degree, the re-

action was stopped by means of evacuating and filling the reactor with nitrogen. The stopcock arrangement also permitted refilling with oxygen in case the total volume to be taken up was more than the capacity of the buret. The readings of the gas buret were corrected to standard conditions for room temperature and pressure.

The electrical properties were measured by Mr. K. G. Coutlee, of these Laboratories.

The infrared spectra were obtained on a Perkin Elmer Model 21 spectrophotometer with the help of Mr. J. P. Luongo of the Bell Telephone Laboratories Analytical Department. Specimens 10 mil thick were used for these studies. A section of each specimen was removed prior to oxidation and used for comparison in the reference beam of the spectrophotometer.

For studies of the effect of metallic copper, freshly cleaned, fine electrolytic dust⁴ (Fisher No. C-431) was thoroughly mixed with the powdered polypropylene before molding.

DISCUSSION

Effect of Oxidation upon Electrical Properties

The effects of increasing amounts of oxidation upon the dielectric constant ϵ and dissipation factor D.F. at 1 kc. and 100 kc. are shown in Table I. The dielectric constant for the polymer was 2.24 at both frequencies before oxidation. The initial dissipation factor was 0.0006 at 1 kc. and 0.0014 at 100 kc. An increase of the dissipation factor to 0.003, or the dielectric constant to 2.28, would render the polypropylene unsuitable for insulation in high-quality telephone cable.

TABLE I
Dielectric Constant and Diffusion Factor of Oxidized Polypropylene

ml. O ₂ /g.	At 1 kc.		At 100 kc.	
	ϵ	D.F.	ϵ	D.F.
None	2.24	0.0006	2.24	0.0014
~0.05	2.26	0.0005	2.26	0.0011
0.042	2.26	0.0016	2.26	0.0016
1.87	2.28	0.003	2.27	0.002
3.39	2.31	0.007	2.31	0.005
6.19	2.30	0.007	2.28	0.006
9.23	2.34	0.015	2.32	0.011

It is interesting to compare points on the oxidation uptake curves (Fig. 2) which correspond to the data in Table I. When 1.87 ml. of oxygen per gram of polymer had been consumed, both ϵ and D.F. had increased to the point where they would begin to adversely affect the transmission properties of a telephone cable. This corresponds approximately to the point at which the autocatalytic portion of the curve (Fig. 2) begins at about

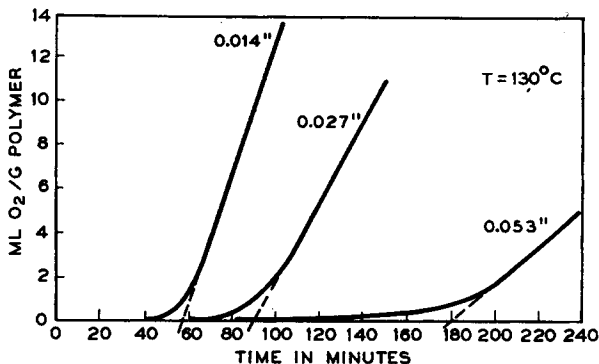


Fig. 2. Oxidation curves for unstabilized polypropylene.

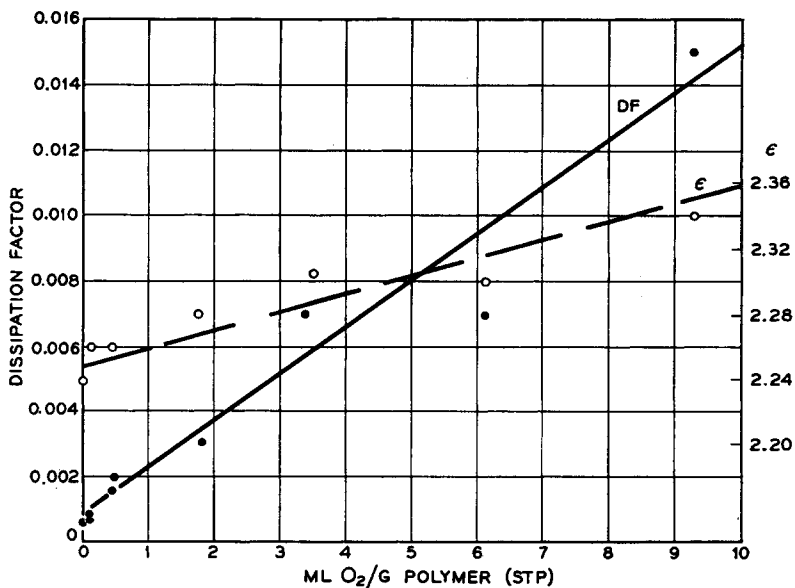


Fig. 3. Effect of O_2 on dissipation factor and dielectric constant of polypropylene at 1 kc.

2-3 ml. of oxygen per gram of polymer. This correspondence is interesting although, perhaps, fortuitous. A plot of the 1 kc. data (Fig. 3) shows that the increase in both ϵ and D.F. are linear with the amount of oxygen absorbed within experimental error.

Infrared Studies

Changes occurring in polypropylene during oxidation were also studied by infrared means. Luongo⁵ followed the increasing hydroperoxide and carbonyl bands with time as polypropylene was allowed to oxidize in air. In our studies the samples were oxidized with known amounts of oxygen.

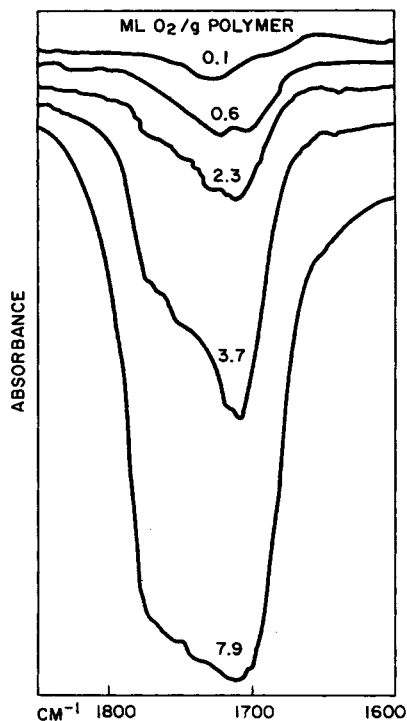


Fig. 4. Infrared spectra of oxidized polypropylenes.

Comparison spectra, with a piece of the original sheet in the reference beam of the spectrophotometer, were then obtained. The hydroperoxide bands could not be clearly established, possibly because these peroxides decomposed before the spectra could be taken. Another factor may have been the proximity of the peroxide bands to the strong 2900 cm.^{-1} CH absorption, which tended to swamp the instrument when comparison spectra were being taken.

The effects upon the carbonyl region are shown in Figure 4. The first sample was allowed to oxidize for about three-quarters of its normal induction time and had taken up 0.1 ml. of oxygen per gram of polymer. A slight increase shown in the carbonyl band at 1730 cm.^{-1} may have been due to an ester or aldehyde.⁶ Increasing the amount of oxidation to 0.6 ml. of oxygen caused the appearance of a band at 1710 cm.^{-1} , probably —COOH . Further oxidation to 2.3 ml. of oxygen per gram of polypropylene intensified this band so that its absorption was stronger than that of the 1730 cm.^{-1} band. A shoulder also appeared at 1775 cm.^{-1} , which is where peroxides of the type CO—O—O—CO— might be expected to absorb.⁶ When a total of 3.7 ml. of oxygen had been consumed by the resin, an almost disproportionate increase in the intensities of all these bands was observed. Figure 2 shows that the autocatalytic portions of the oxidation curves become essentially linear in this region. The absorption of

the carbonyl region became so intense when 7.9 ml. of oxygen per gram had been taken up that the 10 mil. samples were too thick to give good spectra in this region.

It was unfortunate that the strong crystalline polypropylene bands at 995 and 975 cm.^{-1} prevented a study region by this method of the development of unsaturation in the 900–1000 cm.^{-1} .

The hydroxyl regions were also studied by using the original sample in the reference beam. Progressive increases in —OH absorption were also observed but, as mentioned above, swamping of the instrument by the adjacent strong —CH stretching at 2900 cm.^{-1} did not permit detailed examination of the spectra in this region.

Sample Thickness

In their studies of the oxidation of polyethylene, Hawkins et al.¹ found no difference in oxidation rates below the melting point for samples 1 to 10 mils thick, and that above the melting point there are no real differences for samples 10 to 50 mils thick. Burnett,⁷ however, has reported differences in the induction periods of polyethylene for samples of thicknesses.

The effect of thickness on the oxygen uptake curves of these polypropylene sheets at 130°C. can be seen in Figure 2. Both induction times (t_i) and autocatalytic rates vary with thickness of the sample sheet. These data are summarized in Table II.

TABLE II
Oxidation of Polypropylene Sheets

Run no.	Thickness, mils	Area, cm.^2	Wt., g.	t_i , min.	Autocatalytic rate, ml./g./min.
A	13.8	36.0	0.9837	57	0.303
B	12.7	69.1	1.8501	61	0.303
C	27.0	37.7	2.1268	91	0.232
D	53.0	36.1	4.1780	181	0.089
E	50.0	19.9	2.5894	178	0.090

It is immediately apparent that both the induction time t_i and the autocatalytic rate, milliliters of oxygen per gram of polymer per minute, depend on the sample thickness rather than on total weight or total surface area. These t_i 's and rates were quite reproducible. In the preparation of samples for both the infrared and electrical-characteristic studies the induction times corresponded closely to those predicted by this data.

Copper and other metals have been found to promote the oxidative degradation of polypropylene.⁸ The induction times and autocatalytic rates for samples having 1.4% freshly cleaned copper dust are shown in Table III. The induction periods are shortened markedly and the rates are faster. Moreover, there are much greater deviations from the linear

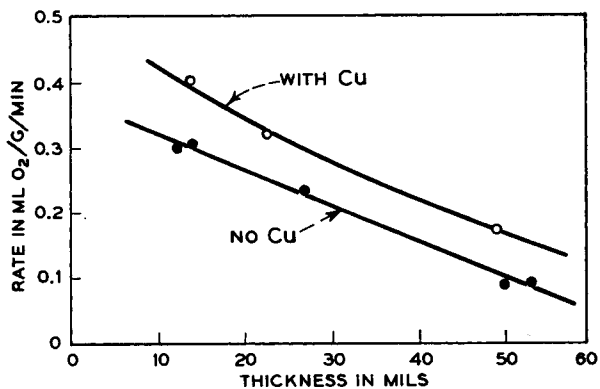


Fig. 5. Autocatalytic rate vs. thickness.

dependence of the t_i 's and rates upon thickness than were found with copper-free samples; this is particularly true in the case of the thinner samples. A plot of the autocatalytic oxidation rates with and without copper are shown in Figure 5.

TABLE III
Effect of Copper (Area 36 cm.²) on Oxidation of Polypropylene

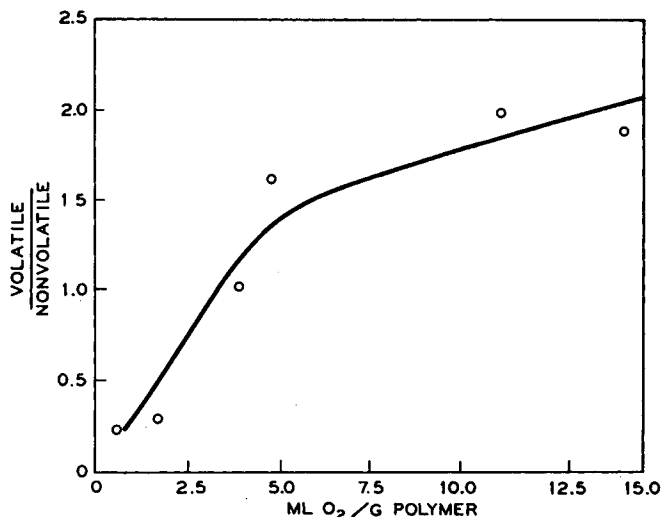
Run no.	Sample thickness, mils	Sample wt., g.	t_i , min.	Rate, ^a ml./g./min.
A ^b	13.8	0.9837	57	0.303
F	14.1	1.0824	12	0.402
G	22.3	1.7669	12	0.320
H	50.0	4.1235	23	0.180

^a During autocatalytic portion.

^b Without copper.

Low Molecular Weight Products

From the increase in the weight of a sample due to the formation of nonvolatile oxygenated products and the weight of the oxygen consumed, the weight of volatile, low molecular weight, oxygenated products can be found. The ratio of the weight of volatile to nonvolatile products retained in the sample is plotted against the volume of oxygen absorbed per gram of polymer in Figure 6. The ratio of volatile to nonvolatile products increases rapidly until about 5.0 ml. of oxygen is consumed, after which it appears to approach a constant value. This is the region in which the oxygen uptake curves become linear. The data in Figure 6 actually indicate an S-shaped curve; however, it is felt that they are not sufficiently accurate to justify drawing a curve through these points thus precisely. In these preliminary studies the nature of the volatile products was not investigated, but it is hoped that such a study will shed new light on the mechanism of polypropylene oxidation.

Fig. 6 Ratio of volatile products vs. O₂.

Effect of Prior Oxidation

An important question to users of polypropylene is the effect of prior exposure to thermal oxidative conditions upon the induction period of the material. To study this factor, samples were exposed to oxygen for various times at 130°C. and then aged at room temperature for various times. The induction times were then determined. A summary of the results is given in Table IV. Samples, heated at the same temperature under nitrogen for comparable lengths of time, gave the normal induction times.

TABLE IV
Preoxidation of Polypropylene^a

Run no.	thickness, mils	t_{po} , min.	Aging, ^a hr.	t_i , min.	$t_{po} + t_i$, min.
H	52	60	68	135	195
I	56	120	48	95	215
J	49	60	92	152	212

^a Average autocatalytic rate, 0.090 ml./g./min.

^b After preoxidation.

The t_i 's of these preoxidized samples were considerably shorter than the 175 to 185 min. normally found with samples of this thickness. Moreover, the sums of the t_i 's and the prior oxidation periods (t_{po}) were only 10–15% longer than the normal induction times. It appears, therefore, that the effects of prior exposures to oxidative conditions are cumulative with respect to the induction periods of polypropylenes. Care should therefore be taken to avoid exposure to air during the processing and compounding of polypropylene, lest the aging qualities of the product be impaired.

The rates of the autocatalytic phase of the reaction were unaffected by the preoxidizing treatments.

GENERAL REMARKS

Because the thickness rather than the total surface area of a polypropylene sample appears to have a major influence on the induction time as well as the autocatalytic rate of thermal oxidation, it seems that during the induction time there is a slow build-up of active centers throughout the body of the polymer, this build-up being controlled by diffusion. When a critical concentration of these active sites is reached, the oxidation becomes autocatalytic. This rapid autocatalytic reaction is also, at least in part, diffusion controlled for an extended period of time.

The active sites exist for some length of time, either in some energy-rich form such as stable peroxides or else as "weak spots," left by the initiation reaction, which have a lower activation energy and thus permit further oxidation. The decay of these centers is slow. They are not formed by thermal conditions alone, since heating under nitrogen for various lengths of time does not appreciably change the induction period of a sample.

The cumulative build-up of active centers or weak spots is undoubtedly partly responsible for the differences we have observed in the induction times of different polypropylene batches. For instance, in one case a pelletized unstabilized polypropylene showed almost no induction period; here the critical concentration of active sites was undoubtedly reached during the pelletizing process.

One may also speculate on the role of copper in polypropylene oxidation. The lack of a linear dependence of the induction time upon sample thickness in the presence of copper indicates that there is no need for the diffusion-controlled build-up of active sites or weak spots having a lower required activation energy. The copper may be breaking down peroxides as soon as they are formed, initiating the oxidation chains, or may function in some manner that lowers the overall activation energy required for oxidation. It is to be hoped that rate studies made at different temperatures will shed more light on this problem.

CONCLUSIONS

As the result of these studies of the beginning phases of isotactic polypropylene oxidation several important conclusions can be drawn. From an electrical standpoint polypropylene is unsuitable for insulation by the time the autocatalytic reaction has started. The induction periods and autocatalytic oxidation rates show a dependency upon sample thickness which is not apparent in the case of polyethylene. From the beginning of the initiation period the oxidation of polypropylene is accompanied by the formation of carbonyl and hydroxyl groups. The loss of volatile, low molecular weight products also occurs in the early stages of oxidation.

Copper not only greatly shortens the induction period of polypropylene but also increases the autocatalytic oxidation rate. It was also found that the effects of exposure to oxidizing conditions for various lengths of time were additive to a considerable degree and resulted in decreased induction times.

References

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Synopsis

The initial stages of isotactic polypropylene oxidation were investigated by oxidizing at 130°C. to various extents up to 10 ml. of oxygen consumed per gram of polymer. The development of infrared absorption bands in the carbonyl regions was followed, as increasing amounts of oxidation occurred. The oxidation uptake curves showed that both autocatalytic rate and induction time depended primarily on the thickness of the sample, contrary to the case of polyethylene. This indicated the initiation process was primarily diffusion controlled for samples of the thickness range studied. The presence of copper shortened the induction times and increased the autocatalytic rate. In this case, the dependency of the induction time on thickness was less. Dielectric data showed that polypropylene became unsuitable electrically at about the point where the autocatalytic oxidation set in. It was also found that the effects of prior exposure to oxidative conditions were cumulative to a considerable extent, and thus resulted in shorter induction times.

Résumé

Les stades initiaux de l'oxydation du polypropylène isotactique ont été étudiés par oxydation à 130°C, à des degrés divers jusqu'à une consommation de 10 ml d'oxygène par gramme de polymère. Le développement de bandes d'absorption infrarouge dans les régions du carbonyle a été suivi lorsque l'oxydation se produisait en quantités croissantes. Les courbes d'oxydation ont montré que la vitesse d'autocatalyse et le temps d'induction dépendent tous deux en premier lieu de l'épaisseur de l'échantillon contrairement au cas du polyéthylène. Ceci indiquait que le processus d'initiation était principalement contrôlé par diffusion pour des échantillons dont l'épaisseur se situe dans le domaine étudié. La présence de cuivre diminuait les temps d'induction et augmentait la vitesse d'autocatalyse. Dans ce cas la dépendance du temps d'induction vis-à-vis de l'épaisseur était moindre. Des données diélectriques ont montré que le polypropylène ne convenait plus électriquement aux environs du point où l'oxydation autocatalytique entre en jeu. On a également trouvé que les effets d'un traitement antérieur à des conditions oxydantes, étaient cumulatifs dans une mesure considérable; il en résulte des temps d'induction plus courts.

Zusammenfassung

Das Anfangsstadium der Oxydation von isotaktischem Polypropylen wurde bei 130°C bei verschiedenem Oxydationsausmass bis zu einem Verbrauch von 10 ml Sauerstoff pro Gramm Polymeres untersucht. Die Entwicklung von Infrarotabsorptionsbanden im Carbonylbereich wurde bei steigender Oxydation verfolgt. Die Kurven für die Sauerstoffaufnahme zeigten, dass sowohl die autokatalytische Geschwindigkeit als auch die Induktionsperiode im Gegensatz zum Polyäthylen, primär von der Proben-dicke abhängen. Das lässt erkennen, dass der Startvorgang bei Proben im untersuchten Dickebereich primär diffusionskontrolliert ist. Gegenwart von Kupfer verkürzte die Induktionsperiode und erhöhte die autokatalytische Geschwindigkeit. In diesem Fall bestand eine geringere Abhängigkeit der Induktionsperiode von der Dicke. Dielektrische Daten zeigten, dass Polypropylen etwa beim Punkt des Einsetzens der autokatalytischen Oxydation elektrisch unbrauchbar wird. Weiters wurde gefunden, dass sich die Effekte einer früheren Einwirkung oxydativer Bedingungen zu einem beträchtlichen Ausmass anhäufen und daher zu kürzeren Induktionsperioden führen.

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