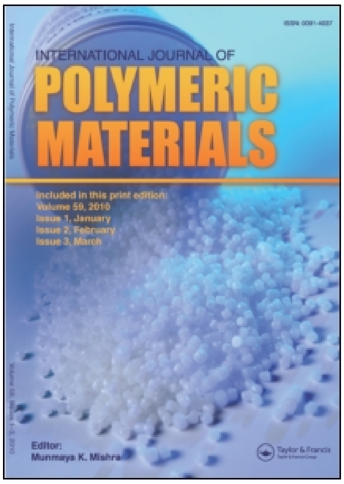

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M. P. Anachkov[a]; S. K. Rakovsky[a]; S. D. Razumovskii[b]
[a] Institute of Kinetics and Catalysis, Bulgarian, Academy of Sciences, Sofia, Bulgaria [b] Institute of Chemical Physics, Moscow, USSR

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Express Method for Determination of the Antiozonants Efficiency

M. P. ANACHKOV and S. K. RAKOVSKY

Institute of Kinetics and Catalysis, Bulgarian, Academy of Sciences, Sofia 1040, Bulgaria

S. D. RAZUMOVSKII

Institute of Chemical Physics, Moscow 117 334, USSR

An express method for determination of the efficiency of antiozonants, based on their inhibiting effect towards ozone degradation of elastomers in solution, is proposed. An efficiency coefficient of the antiozonant was defined as a ratio between the amount of ozone consumed in an elastomer solution containing antiozonant and the amount of ozone that reacted in a solution without antiozonant, through which an equal decrease in the relative viscosity of both the solutions is attained. A stoichiometry coefficient of the protection effect can be determined by monitoring the changes in inhibiting activity of the antiozonants during their ozone conversion. The proposed method was demonstrated in the study of the inhibiting effect of the *N*-phenyl-*N'*-isopropyl-p-phenylenediamine, polimerised 1,2-dihydro-2,2,4-trimethylquinoline and tributhylthiourea antiozonants.

KEYWORDS: Efficiency, antiozonants, express methods, inhibiting, ozone, elastomers

INTRODUCTION

The most widely used methods for characterizing the ozone resistance of rubber products are based on the investigation of different changes of various vulcanisats during their exposition to ozone atmosphere.[1] However, these methods are rather complicated and demand great duration of the experiments. In some cases, the rate constants of the antiozonants reaction with ozone in solution are used for preliminary evaluation of their preserving efficiency.[2] Attempts have been made to find a correlation between the inhibiting effect of some compounds towards ozone degradation of natural and styrene-butadiene rubbers and the ozone resistance of their vulcanisats containing corresponding compounds.[3–5] However, the criteria applied in these works do not provide a sufficiently precise evaluation of the differences in inhibiting activity of the studied antiozonants during the different stages of their ozone conversion.

In the present paper an express method for determination of the efficiency of antiozonants, based on the investigation of their inhibiting effect towards ozone degradation of elastomers in solution, is proposed.

EXPERIMENTAL

Reagents

Ozone was prepared by passing oxygen through a 4–9 kV discharge.

Elastomers

Industrial samples of 1,4-cis-polybutadiene (SKD); 1,4-cis-polyisoprene (SKI-3S) and polychloroprene (Denka M40) rubbers were used. They were purified by three fold precipitation from CCl_4 solutions by excess of methanol.

Antiozonants

The inhibiting efficiency of *N*-phenyl-*N'*-isopropyl-*p*-phenylenediamine (a Bayer product—Antioxidant 4010 NA); polimerised 1,2-dihydro-2,2,4-trimethyl-quinoline (TBTU) was studied.

Methods

Determination of the inhibiting efficiency of the antiozonants towards ozone degradation of elastomers in solution.

Two solutions of equal rubber concentration were prepared and a certain amount of the studied antiozonant was added to one of them. Equal volumes of both solutions were ozonized in one and the same bubbling reactor under constant values of the ozone concentration and of the feeding rate of the ozone-oxygen gas mixture. Gas phase ozone concentrations at reactor inlet ($[O_3]_i$) and outlet ($[O_3]_u$) were measured spectrophotometrically at 254 nm.[6] The amount of consumed ozone (G) was calculated by the equation:

$$G = v([O_3]_i - [O_3]_u)\tau, \tag{1}$$

where τ and v are the ozonation time (s) and the feeding rate of the ozone-oxygen gas mixture (litre/s), respectively. The relative viscosity of the elastomer solutions (η_{rel}) was measured periodically in the progress of reaction and from these data the $\eta_{rel} = f(G)$ dependence was plotted (Figure 1). The efficiency coefficient of the antiozonant was estimated from the relationship:

$$E = \Delta G_2/\Delta G_1, \tag{2}$$

where ΔG_2 is the amount of consumed ozone by the solution containing antiozonant. ΔG_2 values are generally selected in the (0.1–1) q region, where q is the amount of antiozonant in the reactor (mol). ΔG_1 is the amount of reacted ozone in the antiozonant-free solution which changes the relative viscosity provided that $\Delta\eta_{rel(1)} = \Delta\eta_{rel(2)}$. ΔG_1 was determined graphically from Figure 1 if ΔG_2 and $\Delta\eta_{rel(2)}$ were known. Experiments were carried out until the degradation rates of both solutions became equal.

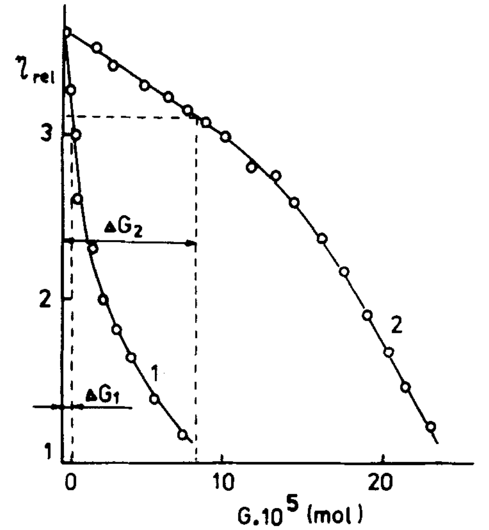

FIGURE 1 Dependence of the relative viscosity η_{rel}) on the amount of reacted ozone (G) for SKD solutions: 1) antiozonant-free; 2) containing 4010 NA.

RESULTS AND DISCUSSION

It is seen from Eq. (1) that E is a relative value and, therefore, a comparison of different coefficients of the antiozonant efficiency is reliable only for similar experimental conditions. ΔG_2 should be considered as a sum of the amount of ozone consumed in a reaction with antiozonant (ΔG_{a0}) and the amount of ozone that has reacted with the C═C bonds of the corresponding rubber (ΔG_1). It is apparent that the higher the rate constant of the reaction of the antiozonant with ozone, the larger the ΔG_{a0} value and hence the inhibiting efficiency is higher. Registration of the changes in inhibiting activity of the antiozonants during their ozone conversion can be used to determine the stoichiometry coefficient of the protection effect.[7] This coefficient defines the maximum number of ozone molecules which are deactivated by one molecule of antiozonant without considerable decrease in its inhibiting efficiency.

The possibilities of the method were demonstrated during the study of the inhibiting effect of the 4010 NA, Flectol H and TBTU antiozonants. Results presented in Table I were obtained under the following conditions: solution volume—15 ml; feeding rate of the ozone-oxygen gas mixture $v = 1.5 \times 10^{-3}$ l/s; $[O_3]_i = 3.1 \times 10^{-5}$ mol/l; antiozonant concentration—3.7×10^{-3} mol/l; concentration of the elastomers solutions of SKD, SKI-3S and Denka M40—0.6, 0.6 and 0.98 g/100 ml CCl_4, respectively.

Table I shows that 4010 NA exhibited the highest inhibiting effect towards the SKD solutions. In addition, its high efficiency was preserved for ΔG_2 values up to $2q$. For $\Delta G_2 = 3q$ the efficiency coefficient was decreased by about 50‰. Further, the degradation rate of solutions 1 and 2 became equal for $\Delta G_2 = 4q$. The inhibiting effect of Flectol H H was much less stronger than that of 4010 NA and

TABLE I

Determination of the efficiency coefficient of antiozonants towards various rubbers

	E			
Antiozonant/rubber	$G/q = 1$	$G/q = 2$	$G/q = 3$	$G/q = 4$
4010 NA/SKD	13.5	13	7.4	1.2
Flectol H/SKD	11	6.2	1	
TBTU/SKD	8	4	1	
4010 NA/SKI-3S	9	8.5	4	1
4010 NA/Denka M40	20	18	10	1.5

its initial value was kept only to $\Delta G_2 = 1q$. TBTU showed the lowest efficiency towards ozone degradation of the SKD solutions.

A very important advantage of the proposed method is the possibility to determine the stoichiometry coefficient of the antiozonant protection effect. Such kind of data cannot be obtained from studies of the ozone resistance of vulcanisats. Moreover, the very high rates of the most antiozonant reactions with ozone and the insufficient knowledge abot the reaction mechanism do not favour a precise determination of the stoichiometry coefficient by measuring the rate constants of the reaction steps.

The data presented in Table I indicate that the nature of the inhibiting effect of 4010 NA was not changed upon ozone degradation of the 1,4-cis-polyisoprene and polychloroprene solutions. However, the corresponding E values decreased in the order Denka M40, SKD, SKI-3S. According to the literature, values of 4×10^3, 6×10^4 and $4 \times 10^5\, \mathrm{l \cdot mol^{-1}\, s^{-1}}$ have been reported for the rate constant of the reaction of ozone with polychloroprene, cis-polybutadiene and cis-polyisoprene in solutions, respectively.[6] It is clear that, under similar conditions, the higher the rate constant, the larger the proportion of ozone is to be expected to react with the corresponding elastomer and, for that reason, the E value should be lower. By comparing the inhibiting effect of one and the same antiozonant towards the ozone degradation of different rubbers in solution, three other factors should be taken into account:

1. Proportion of the degradation processes in the reaction of ozone with the corresponding elastomer. On the basis of a functional group analysis it has been shown that this proportion increases in the order SKD, SKI-3S, Denka M40.[8]

2. Localization of the reaction in a very thin layer around the gas bubbles. It is known that higher rate constants of the rubber with ozone should lead to a lower instantaneous volume of the polymer solution which is to take part in the reaction,[8,9] For that reason the E values, estimated by using the viscosimetric data, should be lower.

3. Presence of a specific interaction of the antiozonant or products of its ozone conversion with the corresponding rubber or products of its ozone conversion.

It is obvious that additional experiments are necessary for a more detailed study of the effect of each one of the above-mentioned factors. However, investigations of this kind come out of the subject of the express method.

Ozone ageing of vulcanisats is a much more complicated process in comparison with the antiozonant-inhibited ozone degradation of rubbers in solution. Nevertheless, the efficiency gradation of the 4010 NA, Flectol H and TBTU antiozonants, established by studying the ozone resistance of vulcanisats,[10] is identical with that determined by the express method. This coincidence is in agreement with the supposition that the preserving effect of the studied antiozonants is mainly determined by the reaction of the antiozonant with O_3 which is competitive to the interaction of an elastomer with ozone. In this connection studies of the antiozonants inhibiting efficiency towards ozone degradation of rubbers in solution can extend our knowledge about the chemical aspects of the antiozonants protection effect.

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