27576
S/190/61/003/009/011/016
B124/B101

15 8520

AUTHORS: Moiseyev, V. D., Neyman, M. B.

TITLE: Molecular weight, number of double bonds, and thermal degradation mechanism of vinyl polymers

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 9, 1961, 1383 - 1388

TEXT: A free-radical chain reaction mechanism is assumed for the thermal degradation of vinyl polymers which consists of the initiation, the depolymerization, the isomerization, the intermolecular chain transfer, and the termination steps. This paper deals exclusively with the thermal degradation of linear high polymers with short side chains (prepared with Ziegler-Natta type catalysts) containing at least 5000 to 10000 units in the chain. The light destruction products were frozen under high vacuum, whereby the polymerization of olefins in the distillate is greatly eliminated. For the degradation mechanism of these polymers, the following facts hold: (1) the chief reason for the decrease in molecular weight during thermal degradation is the chain transfer; (2) the light

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degradation products are distilled off without any change; (3) the light degradation products are formed almost exclusively during isomerization, whereas the monomer forms during depolymerization; (4) the reaction mechanism and, thus, the composition and mean molecular weight of the distillation products remain unchanged during degradation (at constant temperature), as long as the polymer chains are long (mean polymerization degree above $5 - 10\cdot10^3$); (5) nonconsideration of the polymerization of the olefins contained in the solid residue leads to errors in the determination of the chain transfer rate which are, however, small at low degradation degrees, and (6) on the assumption of long kinetic chains, the following relations are found: $w = w_{dep} + w_{iso} + w_{trans}$; $S = (\Delta N_{dep} - \Delta N_{iso} + \Delta N_{trans})/N_o$; ($w_{dep}$ = depolymerization rate, w_{iso} = isomerization rate, w_{trans} = chain transfer rate, S = thermal degradation degree, ΔN_{dep} = number of bonds ruptured on depolymerization, ΔN_{iso} = number of bonds ruptured on isomerization, ΔN_{trans} = number of bonds ruptured on chain transfer, N_o = number of bonds per gram of the polymer at the

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Molecular weight, number...

moment t_o). The number of bonds ruptured on depolymerization equals that of monomer molecules formed: ΔN_{dep} = mon (mon = monomer) (1), and $w_{dep} = (dN_{dep}/dt) = dmon/dt$ (1'). The relation: $w_{iso} = dN_{iso}/dt = (d/dt)(Ol_1 + R_1H) = -(1/\overline{M}_1)(d/dt)(g + g_{mon})$ (2') (Ol_1 = light olefin (up to $C_{30} - C_{40}$), $\overline{M}_1$ = mean molecular weight of the distillate molecule, R_1H = light paraffin (up to $C_{30} - C_{40}$), g = weight of the solid residue at the moment t) holds for the isomerization rate. A general relation: $w_{trans} = -\left\{g_o/\left[\overline{M} - \overline{M}_o(g - g_o)/g_o\right]^2\right\}\left[(d\overline{M}/dt) - (\overline{M}_o/g_o)(dg/dt)\right]$ (6') is derived for the chain transfer rate, where g_o is the weight of the solid residue at the moment t_o, $\overline{M}$ the mean molecular weight of the solid residue at the moment t, and $\overline{M}_o$ the same at the moment t_o. These three quantities can be determined experimentally. From Eq. (6'. and $w_{trans} = (d/dt)(\Delta Ol - R_1H)$ (10') (where $\Delta Ol = Ol_{iso} + Ol_{trans}$) for the chain

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transfer rate, the relation $\bar{M} = \bar{M}_0 \{(g - g_0)/g_0 + 1/[1 + (\bar{M}_0/g_0)(\Delta Ol - Ol_i)]\}$ (11') (Ol = high-molecular (mono) olefin) is derived for the molecular weight of the polymer on the assumption that the molar quantities of olefins and paraffins in the volatile degradation products (with the lightest gases being subtracted) are equal to each other. There are 3 references: 1 Soviet and 2 non-Soviet. The two references to English-language publications read as follows: R. Simha, L. A. Wall, P. J. Blatz, J. Polymer Sci. 5, 615, 1950; H. H. G. Jellinek, Degradation of vinyl polymers, New York, 1955.

X

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics of the AS USSR)

SUBMITTED: December 8, 1960

Card 4/4

28269 S/062/61/000/010/003/018
B117/B101

11,1510

AUTHORS: Neyman, M. B., and Buchachenko, A. L.

TITLE: Investigation of the structure and reactivity of some stable radicals

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 10, 1961, 1742 - 1748

TEXT: The present paper was presented at the general meeting of the Otdeleniye khimicheskikh nauk Akademii nauk SSSR (Department of Chemical Sciences of the Academy of Sciences USSR) in Moscow, June 22, 1961. It contained some new data on stable radicals, their structure, physical properties, and chemical reactions. 40 kinetically stable radicals were obtained by oxidation of phenol derivatives and secondary aromatic amines with organic peroxides, percarbonates, or PbO_2 in benzene or toluene solutions. The radical solutions are colored. Some radicals form colored crystals after evaporation of the solvent. The electron paramagnetic resonance (epr) spectra of the resulting radicals exhibit a fine structure, owing to interaction of the electron spin with the magnetic moments of

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hydrogen and nitrogen nuclei. If the magnetic moment of an unpaired electron interacts only with one proton whose spin is 1/2, the epr spectrum will show a doublet. Interaction of an unpaired electron with two hydrogen atoms of the benzene ring in meta-position results in a triplet structure of the epr spectrum. Interaction of the unpaired electron with three hydrogen atoms of the methyl group in para position gives rise to a quadruplet structure in the epr spectrum. On weak interaction with two hydrogen atoms of the benzene ring in meta-position each line of the quadruplet is split up into three components. The interaction of the unpaired electron with a nitrogen nucleus whose spin is 1, gives a triplet in the epr spectrum. The lines of this triplet are split up into 15 components on weak interaction of the electron with non-equivalent protons of the benzene ring. Even more lines were observable in the epr spectrum on interaction of the dislocated electron with the nitrogen nucleus and with hydrogen nuclei in benzene rings and methoxy groups. In the absence of oxygen, the radicals in question have a long lifetime at room temperature, which permits the investigation of their physical and chemical properties. Some of the radicals can be sublimed in vacuo at ~100°C without decomposition. They form crystals on cold surfaces, and can be determined by the

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epr method. In co-operation with L. G. Gintsberg and B. M. Kovarskaya, absorption spectra of some antioxidants and their radicals were studied in the ultraviolet and infrared. The shift of the absorption bands from the ultraviolet to the visible region, observed during radical formation, explains the coloration of their solutions and crystals. Infrared spectra disclosed that the intensity of the absorption line of hydroxyl at 2.8μ is reduced with a partial formation of the radical and that new lines appear round 6.2μ. The polarographic reduction of kinetically stable radicals in alcohol solutions on an LiCl background was shown to be possible in the potential range of 0.35 - 0.45 v. If the radical contains a polarographically active group, the free valency and this group can be reduced independently at corresponding potentials. The radicals in question cannot dimerize, presumably owing to steric hindrances. They are, however, able to break off the hydrogen from other molecules, e.g. from the solvent, thus forming molecules of the initial phenols. The kinetics of this reaction was studied at different temperatures (90 - 150°C). This reaction was found to be described by a second-order equation. A number of reactions between kinetically stable radicals and molecules of various substances in solutions were examined by the epr

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method. These radicals can be used to investigate the reactivity of various bonds. When kinetically stable radicals are used, their separation from each other and from ordinary molecules is an extremely important problem which can often be solved with the aid of paper chromatography. This was exemplified by the separation and identification of the radicals formed in the oxidation of ionol (2,6-di-tert-butyl-4-methyl-phenol) by this method. Ye. K. Zavoyskiy, Razuvayev, Khidekel, Gorbunova, and M. S. Khloplyankina and the monography by O. A. Reutov: Teoreticheskiye problemy organicheskoy khimii (Theoretical Problems of Organic Chemistry), Izd. MGU, M., 1956, are mentioned. There are 9 figures and 7 references: 3 Soviet and 4 non-Soviet. The two references to English-language publications read as follows: J. K. Becconsall, S. Clough, G. Scott, Trans. Faraday Soc., 56, 459 (1960); C. Cook, J. Organ. Chem., 18, 261 (1953).

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR)

SUBMITTED: June 22, 1961

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21417
S/191/61/000/012/001/007
B101/B110

15 8061

AUTHORS. Dudorov, V. V., Neyman, M. B., Lukovnikov, A. F.

TITLE: Oxidation of polypropylene at high oxygen pressures. The dependence of induction periods on temperature and pressure

PERIODICAL: Plasticheskiye massy, no. 12, 1961, 3-7

TEXT: The oxidation kinetics of polypropylene (PP) is closely related to the problems of thermooxidative PP destruction and grafting of other polymers onto PP. The present paper deals with the examination of the induction period of PP oxidation at a p_{O_2} of 1-120 atm, and 110-140°C. The authors used isotactic PP with a molecular weight of approximately 200,000 separated from the commercial product by a method described by M. V. Mikhaylov et al. (Vysokomol. soyed., 1, 143 (1959)) At about 130°C, 150 kg/cm^2, this PP was used for producing films (0.10 mm thickness, or 10.0 mg/cm^2). The induction period was measured by the apparatus of Fig. 1 (detailed description see Plast. massy, no. 10 (1961)). A certain O_2 pressure was applied to the PP film sample. The pressure change in reaction

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space (2) due to O_2 absorption causes a deflection of membrane (7), which was optically transferred to scale (14) graduated in mm Hg. The induction period was defined as the time in which the pressure in the reaction space dropped by 5 mm. Reproducibility of measurements depended on the preliminary treatment of the reaction vessel and on the conditions of PP films storage. Therefore, a specially treated vessel and films with an induction period of 9.0 ± 0.5 min at 130°C and 20 atm were used for experiments. Special experiments showed that the induction period was not affected by variations of thickness and area of films. At an initial pressure of 100 atm and at 110-140°C, measurement of the pressure drop yielded an apparent induction period τ_{meas} of ~60 min at 110°C, ~[illegible] min at 120°C, and ~15 min at 130°C. Experiments at 140° could only be continued to 60 atm, since inflammation occurred at higher p_{O_2}. The concave shape of the curves showed autocatalytic oxidation to set in at a high p_{O_2}. τ_{meas} decreased until ~40 atm, and increased again at a higher p_{O_2}. This effect is due to an intense separation of volatile products at a high p_{O_2}, which

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almost compensated the pressure drop. The pressure rise caused by volatile products was measured by O_2 removal after short time of action (15-36 min). It followed the linear function $\log\left[p_{max}/(p_{max} - p)\right] = f(t)$; ($t$ = temperature). The constant of pressure rise was determined from this function, and the maximum pressure rise from the curves for pressure rise. The curve for O_2 absorption (Fig. 7) was plotted by means of algebraic addition of the ordinates of pressure drop and rise. Therefrom, the true induction period τ was found. $\tau \ll \tau_{meas}$. Experimental data yielded $\tau = \tau_{\infty} + (\tau_1 - \tau_{\infty})/p$ (1), where τ_{∞} = induction period at $p \to \infty$; $\tau_1 - \tau_{\infty}$ = difference between the induction periods for 1 atm and $p \to \infty$. Since τ_1/τ_{∞} was constant within the experimental errors (1.79-1.90), Eq. (1) was transformed into: $\tau = \tau_{\infty}(1 + 0.85/p)$ (2). $\log \tau$ is a linear function of $1/T$. The temperature coefficient $\gamma = 13{,}500-2300/p$ (3) and the factor of the exponential function $\tau_0 = 1.4 \cdot 10^{-(14 - 3.0/p)}$ (4) were determined. τ was calculated as a func-

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tion of pressure and temperature:

$\tau = 1.4\cdot10^{-14}\exp(13{,}500/T)\exp\left[(1/p)(6.9 - 2300/T)\right]$ (5). Under experimental conditions, 2300/T changes by 8% only. The value of this fraction was calculated for 120°C and substituted in Eq. (5). By resolving Eq. (5) into a series and by using its first two terms, the empirical Eq. (2) is obtained. There are 9 figures, 2 tables, and 7 references: 5 Soviet and 2 non-Soviet. The reference to the English-language publication reads as follows: G. Natta, E. Beati, F. Severini, J. Polym. Sci., 34, no. 127, 685 (1959).

Fig. 1. Diagram of measuring apparatus. (1) Polymer sample; (2) reaction space; (3) thermostat; (4) regulating valves; (5) standard manometer; (6) stop valves; (7) membrane; (8) reaction vessel; (9) space with constant pressure; (10) illuminator; (11) glass; (12), (13) mirrors; (14) measuring scale; (15) funnel.
Legend: (a) Vacuum; (b) oxygen.
Fig. 7. Changes of pressure (curves 1 and 2) and oxygen absorption (curves 1' and 2') during oxidation at 110°C. Pressure: 1 and 1' at 60 atm; 2 and 2' at 120 atm.

Card 4/5

NEYMAN, M.B.; FEKLISOV, G.I.; Prinimal uchastiye: KATYUSHIN, A.A., student

Kinetic tracer method for investigations on the mechanism of complex chemical and biochemical processes. Part 10: Rate constant of the reaction between an acetyl radical and molecular oxygen. Zhur. fiz. khim. 35 no.5:1064-1067 My '61. (MIRA 16:7)

1. Institut khimicheskoy fiziki AN SSSR (for Neyman, Feklisov).
2. Gor'kovskiy gosudarstvennyy universitet (for Katyushin).

(Acetaldehyde) (Carbon oxide)
(Chemical reaction, Rate of)

S/020/61/136/003/022/027
B004/B056

AUTHORS: Neyman, M. B., Miller, V. B., Shlyapnikov, Yu. A., and Torsuyeva, Ye. S.

TITLE: The Dependence of the Induction Period of the Oxidation on the Concentration of the Antioxidant

PERIODICAL: Doklady Akademii nauk SSSR, 1961, Vol. 136, No. 3, pp. 647-650

TEXT: The authors proceed from the fact that the problem of the mechanism of the effect produced by inhibitors of the oxidation, especially the connection between induction period and concentration of an inhibitor is as yet not clear. The present paper therefore studies the effect produced by very low concentrations of oxidation inhibitors upon the induction of the oxidation. According to the chain theory by N. N. Semenov $dn/dt = w_i + \varphi n$ (2) is written down for the oxidation. w_i is the rate of initiation, n is the concentration of the active centers, φ the factor of self-acceleration. With addition of an inhibitor, which breaks

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The Dependence of the Induction Period of
the Oxidation on the Concentration of the
Antioxidant

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off the reaction chain, the reaction follows the system of equations: $dn/dt = w_i + \varphi n - kxn$ (3); $-dx/dt = kxn$ (4). x is the concentration of the inhibitor, k the rate constant of its reaction with the active centers. The following dimensionless variables are introduced: $\nu = n/w_i\tau_0$ (concentration of the active centers); $\kappa = x/w_i\tau_0$ (concentration of the inhibitor); $\Theta = t/\tau_0$ (time). Equations (3), (4) thus assume the form: $d\nu/d\Theta = 1 + a\nu - b\kappa\nu$(5); $-d\kappa/d\Theta = b\kappa\nu$ (6). $a = \varphi\tau_0$; $b = kw_i\tau_0^2$. The discussion of these equations leads to the following result: 1) with $\kappa_0 < a/b$ exponential growth of the active centers; with $\kappa_0 > a/b$ low steady rate of the reaction. Here, $\nu = 1/(b\kappa_0 - a)$ (7) holds for the concentration of the active centers. The induction period is finished as soon as $b\kappa_0 = a$. For the purpose of checking these theoretical assumption, experiments were carried out. The induction period of the thermal oxidation of polypropylene was determined in the presence of various inhibitors of the oxidation (phenolderivatives and aromatic amines). As an example, Fig. 3 shows the course taken by this reaction at

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The Dependence of the Induction Period of the Oxidation on the Concentration of the Antioxidant

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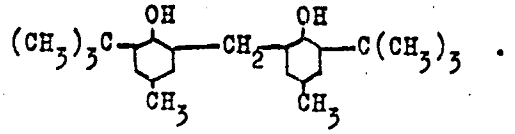
p_{O_2} = 300 mm Hg; 190, 200, and 210°C in the presence of the antioxidant A:



The induction period τ is represented as a function of the concentration x of the inhibitor. From the inclination of the initial sections of the curves $x_0 = k\tau_0/\varphi$ is found. The rate constant k equals 21, 14, and 15 kg/mole.sec. for the temperatures given. For high values of x (steep sections in Fig. 3), an activation energy of about 40,000 kcal/mole is calculated, which corresponds to the activation energies for the oxidation of hydrocarbons. The effectiveness of various oxidation inhibitors may be compared on the basis of k. In this way, the authors proved that at low concentrations N,N'-phenylcyclohexyl-p-phenylendiamine as inhibitor, with polypropylene-oxidation is more effective than the

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The Dependence of the Induction Period of the Oxidation on the Concentration of the Antioxidant

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inhibitor A. There are 3 figures and 7 references: 6 Soviet and 1 British.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR)

PRESENTED: July 29, 1960, by V. N. Kondrat'yev, Academician

SUBMITTED: July 29, 1960

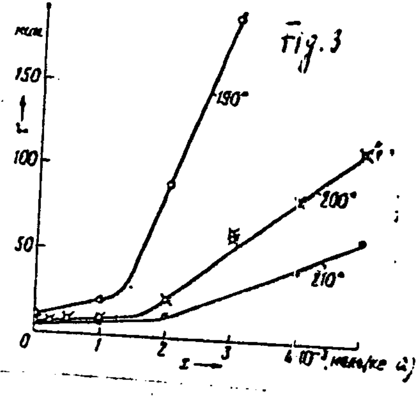

Fig. 3

Legend to Fig. 3: a) mole/kg

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25862
S/020/61/139/004/022/025
B127/B212

11.1510

AUTHORS: Buchachenko, A. L. and Neyman, M. B.

TITLE: Separation of free radicals by the paper chromatography method

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 139, no. 4, 1961, 916-918

TEXT: The authors studied the radicals of 2.6-ditertiary-butyl 4-methylphenol (ionol). Radicals are formed by cracking of hydroxyl hydrogen, which, in turn, may form radicals. Both reactions proceed simultaneously; therefore, the electron paramagnetic resonance spectra overlap. The e.p.r. spectrum of the first ionol radical showed a quadruplet structure with a distance of 11.4 oersteds between the components and an intensity ratio of 1:3:3:1. The quadruplet results from interaction of an unpaired electron with protons of the methyl group in para-position with respect to the oxygen atom. Each quadruplet component was split into three lines of an intensity ratio of 1:2:1 (distance 1.7 oe). This hyperfine structure is caused by the two equivalent protons in meta-position in the

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benzene ring. In order to separate the radicals by paper chromatography, toluene, ethyl alcohol, or carbon tetrachloride were used as mobile phase (flow medium). Best separation was attained with the use of 96% ethyl alcohol. In this case, the band of the ionoloxide solution showed clear separation into two fronts: a lower orange front with Rf = 0, and an upper yellow one with Rf = 1. After drying, each part of the chromatogram was investigated with an ЭПР-2 (EPR-2) spectrometer, and the e.p.r. spectra were recorded. The e.p.r. spectrum of the second ionol radical showed a doublet (1:1; distance 14.5 oe) in solid state, and a triplet (1:2:1;, 8.2 oe) in solution (benzene, toluene, CCl_4). The components of the latter are likewise split into three lines each (1:2:1; 1.8 oe). The doublet-triplet transition was found to be reversible. Thus, an e.p.r. spectrum analysis makes it possible to study the behavior of radicals in solid or liquid states. The authors mention that the above method of paper chromatography may be used also for separating radical and molecule. Here, the first front comprises the radical, and the second, immovable front, the molecule. There are 4 figures and 7 references:

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Separation of free radicals by the...

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B127/B212

3 Soviet-bloc and 4 non-Soviet-bloc. The two most recent references to English-language publications read as follows: Ref. 2: A. J. Beeconsall, S. Clough, G. Scott, Trans. Farad. Soc., 56, 459 (1960); Ref. 6: W. Gordy, C. G. McCornic, J. Am. Chem. Soc., 78, 3243 (1956).

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR)

PRESENTED: April 7, 1961, by V. N. Kondrat'yev, Academician

SUBMITTED: April 3, 1961

Card 3/3

KHIDEKEL', M.L.; BUCHACHENKO, A.L.; RAZUVAYEV, G.A.; GORBUNOVA, L.V.;
NEYMAN, M.B.

Oxidation of β-naphthol and some of its derivatives by peroxide compounds. Dokl. AN SSSR 140 no.5:1096-1099 O '61. (MIRA 15:2)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete im. N.I.Lobachevskogo i Institut khimicheskoy fiziki AN SSSR. 2. Chlen-korrespondent AN SSSR (for Razuvayev).

(Naphthol)
(Peroxides)

NEYMAN, M.B.; MAMEDOVA, Yu.G.; BLENKE, P.; BUCHACHENKO, A.L.

Kinetics of reactions between a tritertiary butyl phenoxy radical and certain hydrocarbons. Dokl.AN SSSR no.2:392-394 My '62.
(MIRA 15:5)

1. Institut khimicheskoy fiziki AN SSSR. Predstavleno akademikom V.N.Kondrat'yevym.
(Hydrocarbons) (Radicals (Chemistry))

НЕЙМАН, М.Б.

4

54999
S/190/62/004/003/01 /023
B124/B101

15.8110

AUTHORS: Kovarskaya, B. M., Strizhkova, A. S., Levantovskaya, I. I., Chabadeh, A. N., Neyman, M. B., Korshak, V. V., Vinogradova, S. V., Valetskiy, P. M.

TITLE: Study of the thermal degradation of condensation resins. III. Thermal degradation of heterochain polyesters (polyarylates)

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 3, 1962, 433-439

TEXT: Thermal degradation of polyarylates on the basis of 4,4'-dihydroxydiphenyl-2,2'-propane (DDP) and terephthalic (polyarylate TD) or isophthalic (polyarylate ID) acids prepared either in a high-boiling solvent (petroleum ether) (TD(s) and ID(s), respectively) or by interfacial condensation (TD(i) and ID(i), respectively) is studied in this paper. The yield points of the polyarylates were: TD(s) ~340°C; TD(i) ~350°C; ID(s) ~260°C; ID(i) ~270°C). Thermal degradation of the mentioned polymers was investigated between 250 and 525°C. Evolution of gas sets in above 400°C, where 0.26-0.42 mole CO, 0.30-0.60 mole CO_2, and 0.06-0.13 CH_4 per mole of the polyarylate structural unit are liberated. The liquid products of thermal

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Study of the thermal ...

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degradation of TD(s) performed at 450°C show absorption bands at 1365, 1385 and 2970 cm^{-1} characteristic of the methyl group, and at 1735 and 1250 cm^{-1} characteristic of the ester bond. The split absorption band at 1735 cm^{-1} indicates the presence of terephthalic acid, whereas the split band at 1600 cm^{-1} shows free DDP to be present. The infrared spectrum of the solid residue of TD(s) after thermal degradation at 450°C for 1 hour does not contain bands which are characteristic of methyl groups, whereas bands characteristic of the ester bond are established in the infrared spectrum of the solid residue exposed to thermal degradation at 500°C for 1 hour. These bands are lacking in the spectrum of the product exposed to thermal degradation at 600°C for 20 minutes. Absorption spectra of the solid residue of TD(s) and DDP in the region of 700 - 900 and 1600 cm^{-1} show that the concentration of phenyl rings increases after degradation leading to the formation of polyphenylene-like structures. These conclusions were confirmed by the ESR spectra of the residues of thermal degradation of TD(s) at 450, 500, and 600°C. A. A. Berlin and L. A. Blyumenfel'd Vysokomolek. soyed., 2, 1494, 1960; Zhurnal strukturnoy khimii 1, 103,

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Study of the thermal... S/190/62/004/003/018/023
B124/B101

1960) are mentioned. There are 7 figures, 1 table, and 11 references: 9 Soviet and 2 non-Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy institut plasticheskikh mass (Scientific Research Institute of Plastics)

SUBMITTED: March 4, 1961.

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39850
S/190/62/004/008/011/016
B101/B138

5,3400

AUTHORS: Shlyapnikov, Yu. A., Miller, V. B., Neyman, M. B., Torsuyeva, Ye. S.

TITLE: Correlations in the effects of inhibitors in oxidation reactions. I. Alkyl phenols

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 8, 1962, 1228-1234

TEXT: The authors studied the effect of 2,6-di-tert.-octyl-4-methyl-phenol (I) and 2,2'-p-methylene-bis-(4-methyl-6-tert.-butyl phenol) (II) on the induction period of the oxidation of isotactic polypropylene. The inhibitor consumption was measured for the induction period at 170 - 220°C in the presence of I, and at 190 - 210°C in the presence of II, according to Vysokomolek. soyed., 2, 1409, 1960. The amount unconsumed was determined by weighing the inhibitor sublimed from the reaction mixture at 200°C. Results: (1) The induction period increases with inhibitor concentration but without linear relation. With I, the

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Correlations in the effects of ...

induction period τ depends on pressure: at 170°C and 0.01 moles I/kg polypropylene, τ was 56 and 32 min at 300 and 600 mm Hg, respectively. (2) The absorption spectra of the oxidation products show that their composition remains unchanged during τ, while their amount is proportional to the decreasing inhibitor concentration. The change in concentration of II during oxidation follows a first-order rule. (3) During τ the decrease in the molecular weight of polypropylene is accelerated as the inhibitor concentration rises. At every polymer chain rupture approximately 5 mols. inhibitor are consumed. (4) τ is considerably shortened by adding I to polypropylene already containing II. (5) The low intensity of the epr signals of I and II suggests that only a small portion of inhibitor is present in the form of free radicals. Conclusions: A large amount of inhibitor is consumed by direct oxidation and chain termination initiated by it, but only a small portion by those not initiated by it. The different behaviors of I and II are due to their different effects on initiation and branching during hydroperoxide decomposition. Rapid and direct oxidation by molecular oxygen is assumed for II. There are 4 figures and 1 table. The most important English-language references are: E. L. Waters, C. J. Busso, Industr. and Engng. Chem., 41, 907, 1949;

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B101/B138

Correlation in the effects of ...

R. H. Rosenwald, J. R. Hoatson, Industr. and Engng. Chem., 41, 914, 1949;
R. H. Rosenwald, J. R. Hoatson, J. A. Chenicek, ibid., 42, 162, 1950.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics of the AS USSR)

SUBMITTED: May 18, 1961

Card 3/3

S/190/62/004/012/015/015
B101/B186

AUTHORS: Alishoyev, V. R., Gur'yanova, V. V., Kovarskaya, B. M., Neyman, M. B.

TITLE: Non-additive effect in the stabilization of polyformaldehyde by additions of polyamides and antioxidants

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 12, 1962, 1887

TEXT: It has been found that a joint addition of polyamide and antioxidant more effectively reduces the evolution of gas in the degradation of polyformaldehyde by thermooxidation than an addition of polyamide or antioxidant alone (Fig.). There is 1 figure.

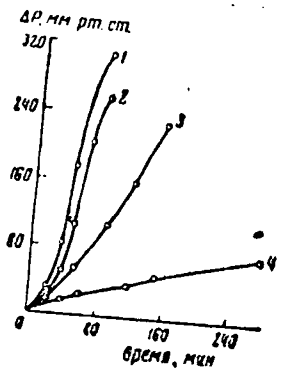
SUBMITTED: June 14, 1962

Fig. Increase of pressure in the oxidation of polyformaldehyde at 200°C, P_{O_2} = 200 mm Hg. (1) Without addition, (2) with polyamide, (3) with antioxidant, (4) with polyamide - antioxidant mixture. Ordinate: ΔP, mm Hg; abscissa: time, min.

Card 1/2

Non-additive effect in the...

S/190/62/004/012/015/015
B101/B186



Card 2/2

NEYMAN, M.B.; PUDOV, V.S.

Effect of inhibitors on the decomposition of polypropylene hydroperoxide. Izv. AN SSSR. Otd.khim.nauk no.5:932 My '62.
(MIRA 15:6)

1. Institut khimicheskoy fiziki AN SSSR.
(Propylene oxide) (Inhibition (Chemistry))

38064
S/191/62/000/006/004/016
B110/B138

15 2121

AUTHORS: Moiseyev, V. D., Neyman, M. B., Kovarskaya, B. M., Zenova, I. Ye., Gur'yanova, V. V.

TITLE: Thermal destruction of condensation resins. Investigation of the thermal destruction of epoxy resins using tagged atoms

PERIODICAL: Plasticheskiye massy, no. 6, 1962, 11-15

TEXT: The destruction mechanism of epoxy resins was investigated by synthesizing epoxy resin ЭД-6 (ED-6), molecular weight 451 (1.8 epoxy groups), with the central carbon atom tagged, in diphenylolpropane. 1 g resin was heated in a glass ampoule, evacuated to $2 \cdot 10^{-2}$ mm Hg, for 1 hr at 300, 400, and 800°C. The destruction products were passed into (1) an empty, exhausted collecting flask cooled by a mixture of acetone and dry ice, and (2) into a similar flask cooled by liquid N_2 and filled with silica gel. To the first was added distilled water, and to the second a saturated solution of NaCl. The gaseous destruction products in the salt solution were examined by absorption gas chromatography (Al_2O_3), and the following were found to be present: (1) $H_2 + CO + CH_4$; (2) C_2H_6;

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(3) C_2H_4; (4) C_3H_8; (5) C_3H_6. The specific activity of the aldehydes in the first collecting flask was determined by A. F. Lukovnikov's method (ZhAKh, 11, 299, (1956)). The percentages by weight for H_2, CO, CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, solid residue, and aldehyde at 300°C were respectively: - ; 1.18; 0.411; 0.025; 0.016; 0.015; 0.068; 98.4; and 0.00023; at 400°C: 0.0008; 1.17; 0.55; 0.039; 0.024; 0.022; 0.055; 98.1; - ; and at 600°C: 1.4; 5.89; 5.27; - ; - ; - ; - ; 87.44; - . Investigation of the activities showed that no losses had occurred. The 5 oe wide signal of paramagnetic resonance (10^{18} paramagnetic particles per g of material) corresponds to the signal of the thermal decomposition products of diphenylol propane. If n is taken as the number of repeating groups in the molecule, then $p = (n + 1)/(2n + 3)$, where p is the molar fraction of diphenylol propane. Then $M = 340 + n\cdot 284$, and $P_e = (86\cdot 100)/(340 + n\cdot 284)$, where P_e is the content (in % by weight) of terminal epoxy groups. Values found for p: from the radioactivity, $p = 0.40$; from the molecular weight, $p = 0.32$; from the content of epoxy groups, $p = 0.38$. At $p = 0.37$, the resin consists chiefly of molecules with $n = 0$ and molecular impurities with $n = 1$. The small fractions of labeled material in the

S/191/62/000/006/004/011
B110/B138

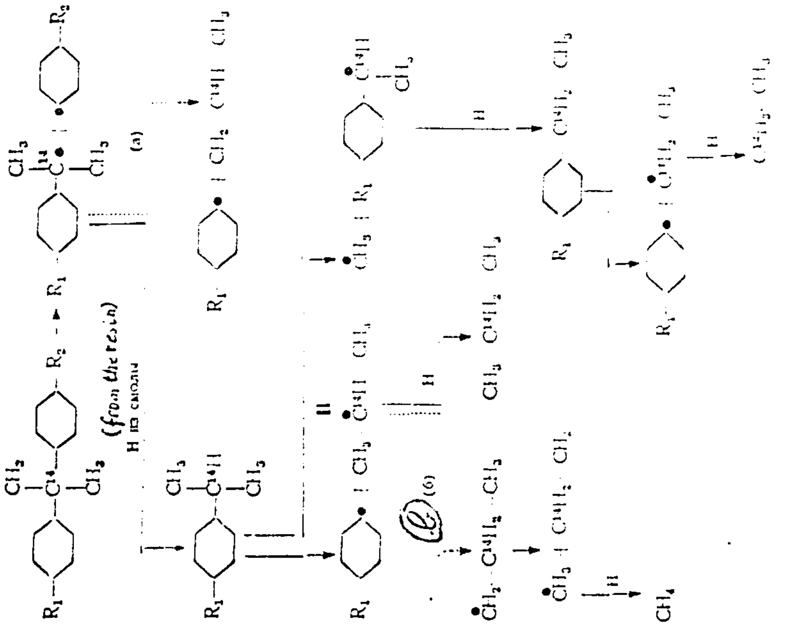
Thermal destruction of ...

decomposition products (propane at 300°C = 4.6 %; at 400°C = [illegible] %) show that the decomposition products derive from the aliphatic part of the resin molecule. The mechanism is presumably

Card 3/5

Thermal destruction of...

S/191/62/000/006/004/016
B110/B138



Card 4/5

The decomposition of radical I by reaction (a) (see Fig.) is inhibited by the stabilizing effect of the phenyl group. The isomerization of radical II by reaction (b) requires ~17 kcal/mole. For this reason, only a small amount of labeled ethylene is formed. As shown also by the paramagnetic electron resonance spectra, the tagged central carbon atom of diphenylol propane participates in the formation of heat-resistant, condensed aromatic and other systems with conjugate double bonds. As the 912 cm^{-1} band of the epoxy group disappears in the infrared spectra of the solid decomposition products of the resin, stable free radicals are formed as reported by M. B. Neyman et al. (Vysokomol. soyed., 1, 10 (1959)). There are 5 figures and 3 tables.

38715

S/191/62/000/007/002/011
B124/B144

15.8.10

AUTHORS: Alishoyev, V. R., Neyman, M. B., Kovarskaya, B. M.

TITLE: Thermooxidative destruction and stabilization of polyformaldehyde

PERIODICAL: Plasticheskiye massy, no. 7, 1962, 11-14

TEXT: The authors sought to obtain kinetic data on thermooxidative destruction and stabilization of polyformaldehyde in laboratory devices and during casting. The same temperature was kept in all parts of the reaction vessel to prevent polymerization. Five cells (Fig. 2) and a weighed portion of about 10 mg were used. Reaction vessel 1 with ground section was connected to the principal part of the apparatus, the weighed portion was added, and an Sn-Pb-Cd-Bi alloy introduced in the curved tube 2; the alloy on melting at test temperature isolated the reaction vessel from the measuring part of the apparatus. The pressure in the reaction vessel automatically balanced itself with that in the measuring part through the action of gases formed in the electrolyzer 3, this being checked in the manometer 4. Thereupon the reaction vessel was evacuated, oxygen was

X

Card 1/~~5~~ 3

introduced through an opening in the alloy, the temperature in the reaction vessel and in the lower part of the curved tube was adjusted to ± 0.5°C by way of a silicone oil thermostat. Fig. 3 shows the results from using a derivatograph on 140 mg of acetylated polyformaldehyde in the course of heating from 20 to 270°C at a rate of 3.3°C/min. The experiments showed that the kinetics of thermooxidative destruction were characterized by the curves for weight losses as well as by those for pressure increase. Whereas in the absence of oxygen the pressure at 145°C rises very slowly with an oxygen pressure of 600 mm Hg it rises at 145°C as follows: $\Delta P = Ae^{\varphi t}$, where $\varphi = 0.044\ \text{min}^{-1}$. In the same experiment, the induction period τ, during which the pressure rises slowly, is 115 min. An analysis showed that HCOH was the main product of thermal destruction, whereas CO, CO_2, H_2O, and H_2 were formed besides HCOH in the thermooxidative destruction. No hydroperoxide was detected analytically. Oxygen takes part in the oxidation of the polymer and stimulates its thermal destruction. The results indicate a self-accelerating chain process with degenerate branching. When either the partial pressure of oxygen or the temperature rises, the autocatalysis

X

Card 2/3

36053

S/063/62/007/002/005/014
A057/A126

15.8000

AUTHOR: Neyman, M.B. Professor

TITLE: Aging and stabilization of polymers

PERIODICAL: Zhurnal vsesoyuznogo khimicheskogo obshchestva imeni D.I. Mendeleyeva, v. 7, no. 2, 1962, 164 - 172

TEXT: Investigations of the mechanism of destruction and stabilization of polymers made in the USSR are discussed, a scheme of oxidation and stabilization of polymers is presented, and some inhibitors are recommended. It is mentioned that in spite of a successful development of these studies many actual problems still have to be solved, especially the stabilization of polymers at high temperature. Two types of aging of polymers are known - destruction and structuration. Destruction effected by thermal oxidation occurs, apparently, according to the mechanism stated by N.N. Semenov as follows: $RH + O_2 = HO_2 + R^\cdot$ initiation (I), $R^\cdot + O_2 = ROO^\cdot$ chain development (II), $ROO^\cdot + RH = ROOH + R^\cdot$ (III) chain development, $ROOH = RO^\cdot + {}^\cdot OH$ branching (IV), $ROO^\cdot + ROO^\cdot = O_2 + ROOR$ rupture of the chain (V). It was observed that thermal oxidation (120-150°C) of isotactic polypropylene follows this scheme, except for reaction (IV) instead of which

X

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S/063/62/007/002/[illegible]/[illegible]
A057/A126

Aging and stabilization.....

the bimolecular reaction ROOH + RH = $RO^{\cdot}$ + H_2O + $R^{\cdot}$ (VI) takes place. Antioxidants (for polypropylene - substituted phenols and aromatic amines) react with peroxide radicals [$ROO^{\cdot}$ + XH = ROOH + $X^{\cdot}$ (VII)], thus breaking the chain reaction and therewith inhibiting destruction of the polymer. However, recent investigations by the present author and co-workers showed that the simple scheme stated by Semenov is not always valid. Thus, increasing temperature decreases the effect of an antioxidant in spite of increasing the concentration of the latter. This and other observations could be explained with the assumption of a second effect of the antioxidant, i.e., initiation of polymer oxidation. Several spectra of paramagnetic electron resonance taken for stabilized substances indicate the formation of radicals by oxidation of the antioxidant used. Studies of the kinetics of reaction between tri-tert-butylphenoxyl and n-decan, 2,4,6-trimethylheptane, or ethylbenzene proved the initiation of polymer oxidation by the reaction of the antioxidant radical and the polymer according to: $X^{\cdot}$ + RH = HX + $R^{\cdot}$ (VIII). Moreover, chain initiation can be effected by reaction with hydroperoxides ROOH + HX = $RO^{\cdot}$ + H_2O + $X^{\cdot}$ (X) or by oxidation of the inhibitor XH + O_2 = $HO_2^{\cdot}$ + $X^{\cdot}$ (XI). The additivity rule of Semenov's mechanism is not valid, because of the well known effect of mutual intensification of the stabilizing property of antioxidant mixtures. Corresponding results were obtained recently by the present author and

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A057/A126

Aging and stabilization.....

co-workers inhibiting polypropylene destruction by binary mixtures of antioxidants. Several studies by other authors showed corresponding results. It depends on the structure of the polymer and antioxidant whether reaction (VIII), (X), or (XI) will control the initiation. Thus, substances destroying the peroxide will increase the stabilizing effect of the antioxidant where (X), and (XI) prevail, while radical-capturing substances will be convenient as admixtures to stabilizers where reaction (VIII) plays the prevailent role. Considering these principles investigations were carried out in laboratories of the NIIPP, IKhF, and VNIIV and the following effective stabilizers found for polyolefines: alkylphenols, aramines, azomethyls, hydrazines, phosphites, and combinations of aramines and phosphites with sulphur-containing compounds. Aging of PVC can be inhibited suitably at low temperatures with polyphenylacetylene, and at high temperatures by polyphenylenes, or polyazophenylenes. The effectiveness of stabilizers against thermal and/or photodestruction apparently depends upon the mobility in the polymer, since high mobility increases the probability of a contact with active radicals and facilitates homogeneous distribution of the stabilizer. In connection herewith was studied recently the diffusion of several stabilizers in polypropylene, polyformaldehyde, and polycaprolactam by the method of labeled atoms in the

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Aging and stabilization.....

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A057/A126

Institut khimicheskoy fiziki (Institute of Chemical Physics). There are 18 figures.

X

Card 4/4

40908
S/191/62/000/010/001/010
B101/B186

15.8200,
15.8530

AUTHORS: ~~Neyman, M. B.,~~ Kovarskaya, B. M., Levantovskaya, I. I., Dral-
yuk, G. V., Yazvikova, M. P., Sidorov, V. A., Kochetkov, V. N.
Trossman, G. M., Tatevos'yan, G. O., Kuznetsova, I. B.

TITLE: Stabilization of polyamide films for agriculture

PERIODICAL: Plasticheskiye massy, no. 10, 1962, 6 - 8

TEXT: Protection of polyamide films, type 54, as used in hothouses and
silos, from effects of photo- and thermooxidation was tested by trying
various additives under various test conditions. The following were added
as ultraviolet light absorbers: 2-hydroxy-4-methoxy-benzophenone OMBΦ
(OMBF) (I), 2-hydroxy-4-alkoxy-benzophenone (a mixture of benzophenones
with various alkoxy groups of the type OC_7H_{15}, OC_8H_{17}, or OC_9H_{19}) (II), and
2-hydroxy-5'-methyl-benzotriazole (Tinuvin) (III). As antioxidants, KI
and copper naphthenate and organic stabilizers of the following type were
used: 1) derivatives of aromatic amines; 2) phenol derivatives; 3) aromatic
oxamines; 4) 2,6-ditert-butyl-4-methyl-phenyl-pyrocatechin phosphite (Ionol).

Card 1/2

ROZANTSEV, E. G.; MAMEDOVA, Yu. G.; NEYMAN, M. B.

Preservation of the free valency in the reduction of the 2,2,6,6-tetramethyl-γ-piperidone-nitric oxide radical according to Kizhner's reaction. Izv. AN SSSR Otd. khim. nauk no.12:2250-2251 D '62. (MIRA 16:1)

1. Institut khimicheskoy fiziki AN SSSR.

[illegible]Piperidone) (Radicals(Chemistry))

MEDVEDEVA, N.I.; NEYMAN, M.B.; TORSUYEVA, Ye.S.

Kinetic tracer method in the study of the mechanism of complex chemical and biochemical processes. Part 11: Rate of formation and consumption of propylene in the cracking of propane. Zhur.-fiz.khim. 36 no.5:1016-1021 My '62. (MIRA 15:8)

1. Institut khimicheskoy fiziki AN SSSR.
(Propene) (Propane) (Cracking process)

S/020/62/143/001/024/030
B101/B147

15806

AUTHORS: Buchachenko, A. L., Khloplyankina, M. S., Neyman, M. B.

TITLE: Formation of inhibitor radicals in polypropylene oxidation

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 143, no. 1, 1962, 146 - 149

TEXT: Isotactic polypropylene powder with an inhibitor dissolved in alcohol was pressed into 100 μ films ($150\ kg/cm^2$, $120^\circ C$ in a CO_2 atmosphere. The inhibitor concentration of the films was $7 \cdot 10^{-2} - 9 \cdot 10^{-2}$ moles/kg. The epr spectrum was taken at 20 - $250^\circ C$ (heating by blowing in hot air). α-naphthol, β-naphthol, binaphthol, 2,6-di-tert-octyl-4-methyl phenol, and diphenyl amine, Ph_2NH, were used as inhibitors. Owing to loss of the H atom in the hydroxyl group, radicals formed with epr spectra consistent with those of the individual inhibitors in the model test. α-naphthol and β-naphthol showed singlets (widths: 3 and 5 oe, respectively). Conjunction of the unpaired electron (UE) on the α-naphthoxyl radical with the π bonds

Card 1/3

S/020/62/143/001/024/030
B101/B147

Formation of inhibitor ...

of the naphthyl ring is more intense than that of the β-radical. The triplet of binaphthol is caused by the reaction of UE with two equivalent protons. Intensive interaction of UE and the protons of the p-methyl group in di-octyl methyl phenol yielded a quadruplet every line of which was split into three lines due to interaction with meta protons. On reacting Ph_2NH with peroxide radicals, Ph_2NO was formed which showed a uniform triplet (width 10.3 oe) caused by reaction of UE with the N^{14} nucleus. Every component was split into 15 lines due to interaction with the o-protons and p-protons of the benzene ring. The hyperfine structure occurring with greater dilution is caused by m-protons. In the initial section, the radical concentration curves were of autocatalytic character. The concentration then increases and goes through a maximum. Comparison with polypropylene powder containing an inhibitor showed its induction period to be considerably reduced. The inhibitor efficiency thus depends on its introduction into the polymer. As compared with α-naphthol, the radical concentration in the presence of β-naphthol was lower according to the lower stability of β-naphthol radicals. The same holds for all above

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Formation of inhibitor ...

S/020/62/143/001/024/030
B101/B147

inhibitors. The majority of radicals are formed by chain rupture during oxidation, a complicated process with degenerate branches. N. B. Neyman's kinetic isotope method might yield quantitative data on the kinetics of inhibitor consumption and O_2 absorption. There are 3 figures and 4 references: 3 Soviet and 1 non-Soviet. The reference to the English-language publication reads as follows: O. L. Harle, J. R. Thomas, J. Am. Chem. Soc., 79, 2973 (1957).

PRESENTED: October 9, 1961, by V. N. Kondrat'yev, Academician

SUBMITTED: October 9, 1961

Card 3/3

41337
S/020/62/146/003/013/019
B101/B144

5.4600

AUTHORS: Kuz'minskiy, A. S., Neyman, M. B., Fedoseyeva, T. S., Lebedev, Ya. S., Buchachenko, A. L., Chertkova, V. F.

TITLE: Conversions of free radicals in gamma-irradiated polyisoprenes

PERIODIAL: Akademiya nauk SSSR. Doklady, v. 146, no. 3, 1962, 611-614

TEXT: The initial stage of cis- and trans-polyisoprene structuration caused by 10-50 Mrad Co^{60} irradiation was studied. The appearance and disappearance of free radicals was ascertained by recording the epr spectrum. An epr spectrum with a signal width of 14 oersteds was observed on trans-polyisoprene after irradiation at room temperature in vacuo. The structure of the radical causing this signal could not be clarified; probably it was formed by separation of a hydrogen atom from the α-methylene group. At -196°C, irradiated trans-polyisoprene showed a broad singlet due to superposition of various radical spectra. If air was admitted to the ampoule at room temperature, the spectrum passed over into a peroxide spectrum. No epr spectrum appeared in cis-poly-

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Conversions of free radicals ... S/020/62/146/003/013/019
B101/B144

number of cross links also proves that with increasing density of the network the mobility of molecular chains is impeded and the recombination of free radicals is rendered difficult. There are 4 figures.

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti (Scientific Research Institute of the Rubber Industry). Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR)

PRESENTED: May 21, 1962, by V. N. Kondrat'yev, Academician

SUBMITTED: May 25, 1962

Card 3/3

5

ACCESSION NR: AP3001579 S/0191/63/000/006/0026/0029

AUTHOR: Akutin, M. S.; Kotrelev, V. N.; Kovarskaya, B. M.; Kostryukova, T. D.; Tarasov, V. V.; Sidnev, A. I.; Rodin, E.; Nitche, O. N.; Neyman, M. B.

TITLE: Casting of polycarbonates under pressure.

SOURCE: Plasticheskiye massy, no. 6, 1963, 26-29

TOPIC TAGS: Diflon, polycarbonate, thermal oxidation

ABSTRACT: The change in molecular weight and mechanical properties of a polycarbonate "Diflon" under laboratory oxidation and on pressure-casting was studied. Polycarbonates are destroyed more rapidly by pressure casting than by thermal oxidation. Apparently, this acceleration is combined with the presence of mechanical destruction. The minimum amount of time and temperature for transforming the polymer to the viscous-flowing state should be used in order to reduce the extent of destruction. Orig. art. has: 9 figures, 1 table and 1 equation.

ASSOCIATION: none

SUBMITTED: 00 DATE ACQ: 01Jul63 ENCL: 00

Card 1/2

L 10623-63 EPR/EPF(c)/EWP(j)/EWT(m)/BDS/ES(s)-2--AFFTC/ASD/SSD--Ps-4/
Pr-4/Pc-4/Pt-4--RM/MAY/WW 85

ACCESSION NR: AP3000687 S/0190/63/005/005/0644/0648 84

AUTHOR: Alishoyev, V. R.; Neyman, M. B.; Kovarskaya, B. M.; Gur'yanova, V. V.

TITLE: Thermooxidative degradation and stabilization of polyformaldehyde

SOURCE: Vysokomolekulyarnyye soyedineniya, v. 5, no. 5, 1963, 644-648

TOPIC TAGS: thermooxidative degradation, degradation, stabilization, polyamide, polyformaldehyde, PFA, 548-27, antioxidant, p-oxineozon, Santovar O, 22-46

ABSTRACT: A method has been developed and used to evaluate the effectiveness of individual polyamide resins (as acceptors of the evolving formaldehyde) and their combination with various antioxidants in stabilizing PFA polyformaldehyde against thermooxidative degradation. The method is based on measurement of the pressure change in a special vessel enclosed in a thermostat containing a PFA sample exposed to oxygen and/or heat. Pressure change versus time curves are plotted and evaluated. Preliminary tests showed that at 145C in the absence of oxygen PFA decomposes very slowly. With oxygen present decomposition is much faster, shows an induction period, and yields formaldehyde, carbon oxides, hydrogen, and water. Screening of polyamide resins "54," "548," and "548-27" by formaldehyde-absorption tests showed that "548-27" is the best formaldehyde acceptor. Antioxidants such as "22-46"

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L 10623-63

ACCESSION NR: AP3000687

(2,2'-methylene-bis(4-methyl-6-tertbutyl)-phonol) or "p-oxineozon" [a p-hydroxy-
phenylnaphthylamine?] in combination with "548-27" were screened by the above
method as additives to PFA at 200C and 200 mm Hg of oxygen. The most effective
antioxidants in combination with "548-27" proved to be "22-46," "p-oxineozon", and
Santovar "0." In the case of the "548-27"/"22-46" combination added to PFA in 2.5%
total concentration the optimum polyamide to antioxidant ratio was 0.6/0.4. This
figure, derived by the pressure-change-curve method, was in good agreement with the
results of control studies of thermooxidation by thermogravimetric and differential
thermal analysis. This work was done at the Scientific Research Institute of
Plastics. Orig. art. has: 8 figures and 1 table.

ASSOCIATION: Nauchno-issledovatel'skiy institut plasticheskikh mass (Scientific
Research Institute of Plastics)

SUBMITTED: 05Oct61	DATE ACQ: 17Jun63	ENCL: 00
SUB CODE: CH,MA	NO REF SOV: 004	OTHER: 007

ch/

Card 2/2

L 10624-63 EPF(c)/EPR/EWP(j)/EWT(m)/BDS/ES(s)-2--AFFTC/ASD/SSD--Pr-4/
Ps-4/Pc-4/Pt-4--RM/MAY/WW

82
81

ACCESSION NR: AP3000688 S/0190/63/005/005/0649/0654

AUTHOR: Kovarskaya, B. M.; Akutin, M. S.; Sidnev, A. I.; Yazvikova, M. P.;
Neyman, M. B.

TITLE: Investigation of the thermooxidative decomposition 15 of a polycarbonate 15

SOURCE: Vysokomolekulyarnyye soyedineniya, v. 5, no. 5, 1963, 649-654

TOPIC TAGS: Diflon, polycarbonate, thermooxidative degradation, thermooxidative decomposition

ABSTRACT: The thermooxidative degradation of the Soviet polycarbonate "Diflon" 15 (mol. wt., 18,000) has been studied. Thermooxidation was carried out at 240 to 300C and 92 to approximately 700 mm Hg of oxygen with equipment described previously by the authors (M. B. Neyman, B. M. Kovarskaya, M. P. Yazvikova, A. I. Sidnev, M. S. Akutin, Vysokomolek. soyed., 3, 602, 1961). It was found that the initial rate of change of pressure in the system, i.e., the oxidation rate (W_0) is directly proportional to the oxygen pressure and increases with temperature according to the law $W_0 = a\ \exp(-E/RT)$, where E = 36,500 kcal/mol. The weight

Card 1/~~3~~2

L 10624-63

ACCESSION NR: AP3000688 0

loss of Diflon at 300C and constant initial oxygen pressure increases linearly with time after a certain initial period; the higher the initial pressure, the greater the loss. Analysis of the degradation products revealed CO_2, CO, H_2 (traces), H_2O, CH_2O, and bis(hydroxyphenyl)propane; hydroperoxides were not detected. It was concluded that the degradation is an autoaccelerating chain reaction with degenerate branchings which are evidently due to hydroperoxide decomposition. The reaction is speeded up by the presence of impurities introduced in the starting materials. Special preliminary purification of Diflon by multiple reprecipitation improved oxidation stability by about 50%. An oxidation mechanism is suggested which shows that oxidation not only gives rise to gaseous products but also alters the structure of the polymer chains in which aldehyde and hydroxy groups accumulate. This is confirmed by the fact that the thermal stability (in the absence of oxygen) of oxidized Diflon is far lower than that of the initial Diflon, owing probably to the decomposition of the aldehyde groups and to additional oxygen-containing groups which facilitate ester bond cleavage. Orig. art. has: 10 formulas and 8 figures.

Scientific Research Institute of Plastics

Card 2/2

AKUTIN, M.S.; KOTRELEV, V.N.; KOVARSKAYA, B.M.; KOSTRYUKOVA, T.D.;
TARASOV, V.V.; SIDNEV, A.I.; RODIN, E.; NITCHE, O.N.; NEYMAN, M.B.

Casting of polycarbonates under pressures. Plast. massy no.6:
26-29 '63. (MIRA 16:10)

L 12720-63 EPF(c)/EWP(j)/EWT(m)/BDS Pr-4/Pc-4 RM/WW
ACCESSION NR: AP3002296 S/0062/63/000/006/1118/1120

66
65

AUTHOR: Buchachenko, A. L.; Sdobnov, Ye. I.; Rafikov, S. R.; Neyman, M. B.

TITLE: Reactivity of diethyl phosphite in radical reactions with tritertiary butyl phenoxyl

SOURCE: AN SSSR. Izv. Otdeleniye khimicheskikh nauk, no. 6, 1963, 1118-1120

TOPIC TAGS: diethyl phosphite, tritertiary butyl phenoxyl, dimerization, kinetic method, degree of solvation

ABSTRACT: The reaction of tertiary butyl phenoxyl with diethyl phosphite proceeds with abstraction of the phosphine hydrogen from monomeric tautomer containing pentavalent phosphorous. The rate constant in benzene at 20 degrees was found to be k sub 1 = 1.2 x 10 sup -25 cc/sec and the equilibrium constant for the dimerization of diethyl phosphite, K = 7.5 x 10 sup -21 cm sup -3. The procedure developed provides a general kinetic method for determining degree of solvation of the reaction center. Orig. art. has: 3 figures.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics); Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR

Card 1/2

ROZANTSEV, E.G.; NEYMAN, M.B.; MAMEDOVA, Yu.G.

Reaction of free organic radicals with Grignard reagents. Izv.AN SSSR.Ser.khim. no.8:1509-1511 Ag '63. (MIRA 16:9)

1. Institut khimicheskoy fiziki AN SSSR.
(Radicals (Chemistry)) (Grignard reagents)

MEDZHIDOV, A.A.; BUCHACHENKO, A.L.; ROZANTSEV, E.G.; NEYMAN, M.B.

Chromatographic separation of the radicals formed during the oxidation of hydrogenated 2,2,4-trimethylquinolines. Izv. AN SSSR Ser.khim. no.10:1713-1717 O '63. (MIRA 17:3)

1. Institut khimicheskoy fiziki AN SSSR.

ROZANTSEV, E.G.; MEDZHIDOV, A.A.; NEYMAN, M.B.

Kinetically stable radicals of the pyrrole series. Izv. AN SSSR Ser.khim. no.10:1876-1877 O '63. (MIRA 17:3)

1. Institut khimicheskoy fiziki AN SSSR.

ACCESSION NR: AP3006755 S/0190/63/005/009/1339/1344

AUTHORS: Neyman, M. B.; Fedoseyeva, T. S.; Chubarova, G. V.; Buchachenko, A. L.; Lebedev, Ya. S.

TITLE: A study of the radicals in irradiated polyformaldehyde

SOURCE: Vy*sokomolekulyarny*ye soyedineniya, v. 5, no. 9, 1963, 1339-1344

TOPIC TAGS: free radical, polyformaldehyde, electron paramagnetic resonance, chain polymer, gamma irradiation, polymer chain/ EPR 2 IKhF spectrometer

ABSTRACT: Structural and kinetic characteristics of free radicals in irradiated polyformaldehyde (PFA) were investigated. Powdered PFA was placed in soldered and evacuated ampules and was subjected to gamma radiation from a Co^{60} source. The study of electron paramagnetic resonance (EPR) radical spectra at low temperatures was conducted on PFA irradiated at 77K with doses of 5×10^6 and 1×10^7 roentgens. Spectra were recorded on the spectrometer EPR-2 IKhF. A special ampule was used for room temperature radiation experiments. The ampule was connected to vacuum equipment to allow varying gas concentrations around the specimens. Means were provided for controlling the ambient air temperature. Test results indicated: 1) two types

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SHLYAPNIKOV, Yu.A.; MILLER, V.B.; NEYMAN, M.B.; TORSUYEVA, Ye.S.

Regularities of the effect of inhibitors in oxidation reactions. Part 2: Mixtures of alkvl phenols with didecyl sulfide. Vysokom. soed. 5 no.10:1507-1512 O '63.
(MIRA 17:1)

1. Institut khimicheskoy fiziki AN SSSR.

NEIMAN, M.B.; LIKHTENSHTEYN, G.I.; KONSTANTINOV, Yu.S.; KARPETS, N.P.;
URMAN, Ya.G.

Thermal oxidative degradation of polypropylene studied by the method of nuclear magnetic resonance. Vysokom.soed. 5 no.11: 1706-1710 N '63. (MIRA 17:1)

1. Institut khimicheskoy fiziki AN SSSR.

BUCHACHENKO, A.L.; NEYMAN, M.B.; SUKHANOVA, O.P.; MAMEDOVA, Yu.G.

Effect of solvents on the reactivity of nitrophenols of different structure in their reaction with the tri-tert-butylphenoxyl radical. Zhur.fiz.khim. 37 no.1:221-224 Ja '63. (MIRA 17:3)

1. Institut khimicheskoy fiziki AN SSSR.

L 15508-63 EPR/EWP(j)/EPF(c)/EWT(m)/ 76
BDS AFFTC/ASD Ps-4/Pc-4/Pr-4 RM/WW 72
ACCESSION NR: AP3006624 S/0076/63/037/009/2077/2081

AUTHOR: Gromov, V. K.; Neyman, M. B.; Vakula, V. L.; Voyutskiy, S. S.

TITLE: Study of the nature of the failure of a polymer-substrate adhesive bond by the method of tagged atoms 19

7

SOURCE: Zh. fizicheskoy khimii, v. 37, no. 9, 1963, 2077-2081

TOPIC TAGS: adhesive bond, adhesive bond failure, bond failure, joint failure, failure, polymer substrate adhesive bond, radiometric method, adhesive, tagged atom, tagged polymer, atactic polypropylene, tagged atactic polypropylene, substrate, nonradioactive atactic polypropylene, sheet silicate glass, copper foil, stripping test, adhesion testing machine, TsNIKZ adhesion testing machine, bond strength, radioactivity, substrate radioactivity, bonding time, bonding temperature, micromosaic type failure

ABSTRACT: The failure of polymer—substrate adhesive bonds has been studied by a highly sensitive radiometric method developed

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L 15508-63
ACCESSION NR: AP3006624 2

by the authors employing a tagged polymer. Atactic polypropylene (molecular weight, 3 x 10^4) with tagged tertiary C atoms was used as an adhesive and nonradioactive atactic polypropylene, sheet silicate glass, or copper foil, as a substrate. Stripping tests on percale strips coated with the adhesive were conducted with a TsNIKZ adhesion testing machine; the radioactivity of the stripped substrates was then measured. The results are given in the form of tables and graphs. The fact that all stripped substrates were radioactive indicates that after bond failure a certain amount of adhesive remains on the substrate. Radioactivity measurements showed that the quantity of adhesive remaining on the substrate increased with an increase in the time and temperature of contact between adhesive and substrate during specimen preparation. It is assumed that: 1) the adhesive remaining as nonpolymeric substrate is distributed in the form of "islets" rather than as a uniform layer and that in such case bond failure is "micromosaic" in type; 2) in the case of polymeric substrates of a higher molecular weight with three-dimensional or supermolecular network structures

Card 2/3

L 15508-63

ACCESSION NR: AP3006624

2

and considerable intermolecular forces, smaller quantities of the adhesive will remain on the substrates. Orig. art. has: 2 figures, and 2 tables.

ASSOCIATION: Akademiya nauk SSSR. Institut khimicheskoy fiziki (Academy of Sciences SSSR, Institute of Chemical Physics); Moskovskiy institut tonkoy khimicheskoy tekhnologii imeni M. V. Lomonosova (Moscow Institute of Fine Chemical Technology)

SUBMITTED: 17Oct63 DATE ACQ: 30Sep63 ENCL: 00

SUB CODE: CH, PH NO REF SOV: 005 OTHER: 008

Card 3/3

S/020/63/148/001/019/032
B101/B186

AUTHORS: Buchachenko, A. L., Gur'yanova, Ye. N., Kalashnikova, L.A., Neyman, M. B.

TITLE: Dipole moments of the diphenyl nitrogen oxide radical and of the diphenyl hydroxylamine molecule

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 148, no. 1, 1963, 95-96

TEXT: The molar polarization P_{∞} at infinite dilution and the molar refraction R_D for the D line of sodium of $C_6H_5-\underset{O\cdot}{\underset{|}{N}}-C_6H_5$ (I) and of $C_6H_5-\underset{OH}{\underset{|}{N}}-C_6H_5$ (II) were determined in benzene at 25°C. The dipole moment was calculated according to $\mu = 0.22\sqrt{P_{\infty} - R_D}$. Data found for I: m.p. = 64°C, $P_{\infty} = 240.8$, $R_D = 55.8$, $\mu = 3.0 \cdot 10^{-18}$, and for II: m.p. = 60°C, $P_{\infty} = 91.8$, $R_D = 56.9$, $\mu = 1.5 \cdot 10^{-18}$. The discussion of these μ values leads to the conclusion that no additivity exists and that μ for I cannot

Card 1/2

L 13700-63 EWP(j)/EPF(c)/EWT(m)/BDS Pc-4/Pr-4 RM/WW

ACCESSION NR: AP3003521 S/0020/63/151/001/0148/0150

AUTHORS: Shlyapnikov, Yu. A.; Miller, V. B.; Neyman, M. B.; Torsuyeva, Ye. S.

TITLE: Participation of inhibitor in degenerate branching of a chain

65

64

SOURCE: AN SSSR. Doklady, v. 151, no. 1, 1963, 148-150

TOPIC TAGS: inhibitor, oxygen pressure, oxidizing reaction, chain branching

ABSTRACT: The author investigated the influence of the inhibitor "monophenol" on the quantity of critical concentration of another inhibitor "biphenol". It is shown that the factor of self-accelerating oxidizing reaction of high-molecular carbohydrate depends on the oxygen pressure and on the concentration of the "monophenol" inhibitor. The growth of the self-accelerating oxidizing reaction factor in the presence of the inhibitor "monophenol" is explained by the participation of the inhibitor in the act of degenerate branching of chains. The paper was presented by Academician N. N. Semenov on 11 March 1963. Orig. art. has: 11 formulas and 2 figures.

ASSOCIATION: Inst. of Chemical Physics, Academy of Sciences

Card 1/2

NEYMAN, M.B., otv. red.

[New developments in chemistry] Novoe v khimii; sbornik
statei. Moskva, Nauka, 1964. 361 p. (MIRA 17:12)

1. Akademiya nauk SSSR.

L 24517-65 EPA(s)-2/EWT(m)/EPF(c)/EPR/EWP(j)/T Pc-4/Pr-4/Ps-4/Pt-10 WW/RM

ACCESSION NR AM5002549 BOOK EXPLOITATION S/ 41
39
134/

Neyman, M. B. (Doctor of Chemical Sciences, Professor) ed.

Destruction and stabilization of polymers (Stareniye i stabilizatsiya polimerov), Moscow, Izd-vo "Nauka", 1964, 330 p. illus., biblio. Errata slip inserted. 3,500 copies printed. (At head of title: Akademiya nauk SSSR. Institut khimicheskoy fiziki).

TOPIC TAGS: degradation reaction, aging process, stabilization, polyolefin, polyvinylchloride, vinylchloride copolymer, polyamide, synthetic rubber, synthetic resin

TABLE OF CONTENTS:

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L 24517-65
ACCESSION NR AM5002549

2

L 27873-65 EPA(s)-2/EWT(m)/EPF(c)/EPR/EWP(j)/T Pc-4/Pr-4/Ps-4/Pt-10 WW/GS/RM

ACCESSION NR: AT4049841 S/0000/64/000/000/0033/0036 52 52 B+1

AUTHOR: Kovarskaya, B. M.; Zhigunova, I. Ye.; Slonim, I. Ya.; Urman, Ya. G.; Neyman, M. B.

TITLE: Investigation of the degradation products and the change in mobility of molecular chains during the thermal degradation of polycarbonate 15

SOURCE: Khimicheskiye svoystva i modifikatsiya polimerov (Chemical properties and the modification of polymers); sbornik statey. Moscow, Izd-vo Nauka, 1964, 33-36

TOPIC TAGS: polycarbonate, polyarylate, infrared spectroscopy, EPR spectrum, pyrolysis, thermal degradation / Diflon

ABSTRACT: It was found that the polycarbonate "Diflon", with a structure similar [illegible] polyarylates based on diphenylolpropane and terephthalic (or iso-

L 27813-65

ACCESSION NR: AT4049841

Infrared spectra of polycarbonate and of the solid residue after degradation at 500C showed that the absorption bands of the CH_3 group (2970, 1365, 1385 cm^{-1}) which are present in the initial polycarbonate are missing in the solid residue, and that the intensity of the absorption bands of the groups $C=O$ and $C-O-C$ (1780 and 1259 cm^{-1}) decreases. The increase in the intensity of absorption at 1600 and 800 cm^{-1}, corresponding to the benzene ring, in the solid residue shows that the residue contains more phenyl rings after degradation. The change in the structure and molecular mobility during degradation of polycarbonate was also investigated by nuclear paramagnetic resonance spectra. Here, the width of the line depends on the degree of mobility of the molecular group containing the resonant ring. At a temperature higher than 150C and lower than -130C, for the initial polycarbonate, a composite signal is seen which consists of two components: a narrow and a wide band. Two regions of decreased width of the line from -150 to -50C and from 150 to 170C are found for the initial polycarbonate. The narrowing of the EPR line at low temperatures is due to the mobility of the CH_3 groups in the polymer. This

L 27873-65

ACCESSION NR: AT4049841 /

ASSOCIATION: Nauchno-issledovatel'skiy institut plasticheskikh mass (Plastics scientific research institute)

SUBMITTED: 22May62 ENCL: 00 SUB CODE: GC, NP

NO REF SOV: 003 OTHER: 004

Card 3/3

L 27874-65 EPA(s)-2/EWT(m)/EPF(c)/EPR/EWP(j)/T Pc-4/Pr-4/Ps-4/Pt-10 RPL
WW/GS/RM

ACCESSION NR: AT4049845 S/0000/64/000/000/0086/0092

54
53
B+1

AUTHOR: Moiseyev, V. D.; Neyman, M. B.; Suskina, V. I.

TITLE: Rates of depolymerization, isomerization and chain transfer during the thermal degradation of polypropylene

SOURCE: Khimicheskiye svoystva i modifikatsiya polimerov (Chemical properties and the modification of polymers); sbornik statey. Moscow, Izd-vo Nauka, 1964, 86-92

TOPIC TAGS: polypropylene, depolymerization, isomerization, chain transfer, thermal degradation, dissociation energy, activation energy, intrinsic viscosity

ABSTRACT: Two fractions (I with η_0=3.2 and II with η_0=2.9) of a low-pressure polypropylene were tested, and experimental data were obtained on weight loss,

L 27874-65

ACCESSION NR: AT4049845 0

I after heating for 180 min. at 200, 250, 265, 280, 290 and 300C became 3.2, 2.8, 2.6, 2.2, 1.9 and 1.7, respectively. At 200C the intrinsic viscosity remained unchanged; at 300C, the gas evolution was low and the weight loss insignificant. At 345C the polymer lost less than 3% of its weight, and the average molecular weight of the evolved gases was close to 44. The kinetic data obtained show that during the thermal degradation of polypropylene, together with other processes, polymerization of the degradation products takes place. For polymer I, on the basis of the points of the diagram corresponding to temperatures of 315, 330 and 345C, Q (dissociation energy) = 18.0 kcal/mole; for polymer II at the same temperatures, Q = 19.7 kcal/mole. Tabulated data are given for the solution of the problem of the case of the high rate of thermal degradation. The total rate of thermal degradation of polypropylene is equal to the sum of the rates of depolymerization, isomerization and chain transfer. At 345C W has a value of 10^{15}-10^{16} ruptured bonds per g. sec. It was concluded for polypropylene that the high rate of thermal degradation of polymers cannot be explained by the concepts of the normal [illegible] at the same time the concept of weak bonds meets certain

L 27874-65

ACCESSION NR: AT4049845

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Chemical physics institute, AN SSSR)

SUBMITTED: 16Jun62 ENCL: 00 SUB CODE: OC,GC

NO REF SOV: 004 OTHER: 009

Card 3/3

L 34141-65 EWT(m)/EPF(c)/EWP(j) Pc-4/Pr-4 GS/RM
ACCESSION NR: AT4049847 S/0000/64/000/000/0106/0109
25
22
27
B
1

AUTHOR: Shlyapnikov, Yu. A.; Miller, V. B.; Neyman, M. B.; Torsuyeva, Ye. S.

TITLE: The kinetics of the effect of inhibitors in oxidation reactions. III. Inhibitor 2,2'-thio-bis-(4-methyl-6 tert.-butylphenol)

SOURCE: Khimicheskiye svoystva i modifikatsiya polimerov (Chemical properties and the modification of polymers); sbornik statey. Moscow, Izd-vo Nauka, 1964, 106-109

TOPIC TAGS: polypropylene, isotactic polymer, oxidation inhibitor, alkylphenol, thiobiphenol, polymer oxidation, biphenol

ABSTRACT: The oxidation of linear isotactic polypropylene was investigated at about 200C in the presence of the inhibitor 2,2'-thio-bis-(4-methyl-6-tert.-butylphenol), m.p. 83-84C, abbreviated as thiobiphenol. The dependence of the

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L 34141-65

ACCESSION NR: AT4049847

period was investigated only at 200C at initial inhibitor concentrations of 0.015 and 0.030 mole/kg. The rate constants of thiobiphenol consumption calculated

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L 34141-65
ACCESSION NR: AT4049847

2

equation describing the consumption of one inhibitor in the oxidizing mixture containing two inhibitors of the same type is given. In a mixture of these two inhibitors, 2,2'-thio-bis-(4-methyl-6-tert.-butylphenol) is consumed more slowly. and 2,2'-methylene - bis-(4-methyl

Orig. art. has: 4 figures and 5 formulas.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Chemical physics institute, AN SSSR)

SUBMITTED: 07Jul62 ENCL: 00 SUB CODE: OC, GC

NO REF SOV: 005 OTHER: 000

L 34116-65 EPA(s)-2/EWT(m)/EPF(c)/EPR/EWP(j)/T Pc-4/Pr-4/Ps-4/Pt-10 WW/[illegible] RM

ACCESSION NR: AT4049855 S/0000/64/000/000/0156/0159 34

33

B+1

AUTHOR: Goglev, R. S.; Neyman, M. B.

TITLE: Thermo-oxidative degradation of polyethylene oxide

SOURCE: Khimicheskiye svoystva imodifikatsiya polimerov (Chemical properties and the modification of polymers); sbornik statey. Moscow, Izd-vo Nauka, 1964, 156-159

TOPIC TAGS: polyethylene oxide, thermal degradation, propylgallate, aromatic amine, oxidative degradation, polymer oxidation, antioxidant

ABSTRACT: The induction period of the oxidation of polyethylene oxide (PEO) was investigated as a function of temperature and oxygen pressure. The initial product (molecular weight 25000) was obtained by bulk polymerization of ethylene

ature and oxygen pressure, up to 250 mm Hg. The activation energy of

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L 34116-65
ACCESSION NR: AT4049855

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was calculated at 33,000 cal/mole. The data obtained for the retardation of oxidation of PEO by antioxidants are tabulated. The induction period at a concentration of antioxidant of 9.5 x 10^{-3} mole/kg, 135C and P_{O_2}=340 mm was chosen as characteristic for evaluating the effectiveness of stabilizers. The plotted and tabulated data show that at the given temperature and 2 figures.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Chemical physics institute, AN SSSR)

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L 34116-65
ACCESSION NR: AT4049855

SUBMITTED: 15Oct62 ENCL: 00 SUB CODE: OC

NO REF SOV: 010 OTHER: 003

Card 3/3

ACCESSION NR: AP4018159 S/0191/64/000/003/0014/0017

AUTHORS: Levantovskaya, I.I.; Kovarskaya, B.M.; Neyman, M.B.; Rozantsev, E.G.; Yazvikova, M.P.

TITLE: Inhibiting the thermal oxidative destruction of polyamides with aromatic amines and radical type stabilizers

SOURCE: Plasticheskiye massy*, no.3, 1964, 14-17

TOPIC TAGS: polyamide, thermal oxidation, oxidation inhibition, antioxidant, phenyl beta naphthylamine, piperidine nitric oxide, piperidone nitric oxide, radical type stabilizer, induction period

ABSTRACT: The inhibition of thermal oxidation of polyamides with phenyl-beta-naphthylamine and with the free radical type stabilizers 2,2,6,6-tetramethylpiperidone nitric oxide and 2,2,6,6-tetramethyl-4-ethyl-4-hydroxypiperidine nitric oxide was investigated. The radical stabilizers display marked inhibition of thermal oxidation. Less than half of the original amount of aromatic amine is spent during the induction period in inhibiting polyamide thermal oxidation; inhi-

Card 1/2

ACCESSION NR: AP4018159

bition of oxidation at the end of the induction period apparently depends on the remaining unspent antioxidant. Unlike the aromatic amines, the free radical inhibitors retard the oxidation of polyamides until they are completely consumed. At the end of the induction period the rate of oxidation with these radical inhibitors approaches the rate of oxidation of the uninhibited polymer. Orig. art. has: 8 figures and 2 formulas.

ASSOCIATION: None

SUBMITTED: 00 DATE ACQ: 27Mar64 ENCL: 00

SUB CODE: CH NR REF SOV: 008 OTHER: 000

Card 2/2

ACCESSION NR: AP4042869 S/0062/64/000/007/1178/1184

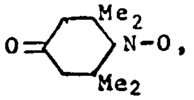
AUTHOR: Neyman, M. B.; Rozantsev, E. G.

TITLE: The use of stable radicals as antioxidants

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 7, 1964, 1178-1184

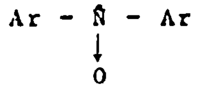
TOPIC TAGS: antioxidant, free radical, nitroxide, acetoneamine, polymer stabilization, polymeric material, polyformaldehyde stabilization, polyamide 68 stabilization, polypropylene stabilization

ABSTRACT: The authors had previously found that a new type of antioxidant — the nitroxides — terminate the oxidation chain reaction without increasing the probability of branching of the reaction chains. These new antioxidants contain a -N-O· group with a free-radical valence. The simplest nitroxide was synthesized from acetone and ammonia by the catalytic oxidation of the intermediate triacetoneamine to the structure:



ACCESSION NR: AP4042869

where Me represents the CH_3 group. Further, a series of aromatic nitroxides of the type



$$\mathrm{Ar} - \underset{\substack{\downarrow \\ \mathrm{O}}}{\dot{\mathrm{N}}} - \mathrm{Ar}$$

was prepared, where Ar designates a substituted aromatic radical with alkyl and alkoxy substituents. The previous experiments of the authors, in which ethylbenzene was oxidized by air in the presence of azobisisobutyronitrile used as the chain initiator, indicated that the nitroxide radicals of the triacetoneamine series practically do not react with the formed hydroperoxide radicals ROO. However, when oxygen was excluded and replaced by helium, the reaction of nitroxide free radicals with hydrocarbon radicals R• took place. Similar behavior of nitroxide radicals was observed also in the oxidation of isotactic polypropylene in films; it was found that nitroxide radicals accelerated the decomposition of hydroperoxide (which results in branching of the chain) only 30%, while the aromatic amines which are also used as antioxidants accelerated this

ACCESSION NR: AP4042869

decomposition by 30—40 times. Experiments with the oxidation of polyamide-68 at 160C and 200 mm Hg oxygen pressure indicated that bis-2,2,6,6,-tetramethyl-4-ethyl-4-hydroxypiperidine nitroxide produced an induction period of approximately 200 min, i.e., equal to that produced by one of the most effective antioxidants — Neozone D. In experiments involving the thermooxidative decomposition of polyformaldehyde the nitroxide radical was to be combined with a polyamide to bind the evolving formaldehyde. An increase in nitroxide antioxidant concentration produces an increase in the induction period, and saturation is attained after the initial increase of the effect. The authors state that the effectiveness of the nitroxide antioxidants depends on the structure of the compounds; however, the reaction found by the authors for their synthesis of nitroxides makes it possible to prepare a variety of these antioxidants, including compounds with low volatility and high antioxidant effectiveness. Some water-soluble nitroxides might be of interest for biochemical studies; aromatic nitroxides are promising antioxidants for rubber. Orig. art. has: 11 figures.

Card 3/ 4

ACCESSION NR: AP4042869

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics AN SSSR)

SUBMITTED: 20Feb64	ATD PRESS: 3070	ENCL: 00
SUB CODE: OC, MT	NO REF SOV: 016	OTHER: 007

Card 4/4

L 8448-65 EWT(m)/EWP(o)/EWP(j)/T Pc-4/Pr-4 RPL/SSD/AFWL WW/JFW/RM/WH
ACCESSION NR: AP4044707 S/0062/64/000/008/1518/1521

AUTHOR: Neyman, M. B.; Mayranovskiy, S. G.; Kovarskaya, B. M.; Rozantsev, E. G.; Gintsburg, E. G. B

TITLE: Polarographic study of certain 1-oxide free radicals

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 8, 1964, 1518-1521

TOPIC TAGS: electrochemical reduction, polarographic analysis, 1 oxide free radical, free radical reduction, radical protonization

ABSTRACT: Electrochemical reduction of the 2,2,6,6-tetramethylpiperidonyl 1-oxide radical (I) on a dropping mercury electrode has been studied and compared with that of the 2,2,6,6-tetramethylpiperidino 1-oxide radical (II) to get additional data on the properties and feasibility of polarographic analysis of recently discovered stable 1-oxide free radicals. The effects of pH, concentration, and

utions at 25C. It was shown that in the 1—13 pH range both I and II

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L 8443-65
ACCESSION NR: AP4044707

2

are reduced irreversibly to the corresponding hydroxylamine derivatives and produce a single-electron, single-step diffusion wave. The height of the wave is independent of pH, but $E_{1/2}$ shifts to negative potentials with increase in the pH of solution. $E_{1/2}$ remains nearly constant only in a narrow, neutral pH range. The pH dependence of

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry, Academy of Sciences SSSR); Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics, Academy of Sciences SSSR)

Card 2/3

L 8448-65

ACCESSION NR: AP4044707

SUBMITTED: 03Jan64 ATD PRESS: 3097 ENCL: 00

0

SUB CODE: IC, OP NO REF SOV: 006

NO REF SOV: 006 OTHER: 002

Card 3/3

L 14507-65 EPA(s)-2/EWT(m)/EPF(c)/EPR/EWP(j)/T Pc-4/Pr-4/Ps-4/Pt-10 ASD(m)-3/
ASD(p)-3/AFTC(a)/RAEM(a) WW/RM

ACCESSION NR: AP4048202 S/0191/64/000/011/0015/0016

AUTHOR: Strizhkova, A. S., Kovarskaya, B. M., Neyman, M. B. B

TITLE: Thermooxidative degradation of polyacrylic ester 15

SOURCE: Plasticheskiye massy*, no. 11, 1964, 15-16

TOPIC TAGS: polyacrylic ester, thermooxidative degradation, antioxidant, stabilizer, polymer autooxidation

ABSTRACT: The authors studied the thermooxidative degradation of the simplest polyacrylic ester, TGM-3. The purified ester, in powder form, was polymerized in the presence of 1% benzoyl peroxide at 100-110C for 30 minutes after which the oxidative degradation was followed using the static apparatus described earlier. The degree of

ly heat-stable in the presence of oxygen;

Card 1/2

L 14307-65

ACCESSION NR: AP4048202

presence of an induction period reveals the autocatalytic character of this thermooxidative reaction. The kinetics of the accumulation of hydroperoxides during the oxidation of polyacrylic ester was studied by the iodometric method at 130C (pO_2 = 200 mm Hg); here, the maximum peroxide concentration corresponds to the maximum oxidation rate. It can be concluded that the oxidation of polyacrylic ester proceeds as a chain reaction with the formation of hydroperoxide, the decomposition of which leads to degenerated branching, which explains the autooxidative character of the process. The effect of different stabil sample. Orig. art. has: 5 figures.

ASSOCIATION: None

SUBMITTED: 00 ENCL: 00 SUB CODE: OC, MT

NO REF SOV: 004 OTHER: 000

Card 2/2

ACCESSION NR: AP4017634 S/0190/64/006/002/0241/0246

AUTHORS: Fedoseyeva, T. S.; Kuz'minskiy, A. S.; Neyman, M. B.; Buchachenko, A. L.; Lebedev, Ya. S.; Chertkova, V. F.

TITLE: Effect of three-dimensional network on free radical annihilation process in elastomers

SOURCE: Vy*sokomolekulyarny*ye soyedineniya, v. 6, no. 2, 1964, 241-246

TOPIC TAGS: free radical, sodium-butadiene, thermal vulcanizate, EPR spectra, irradiated specimen, chain segment, activation energy, pre-exponential factor

ABSTRACT: The kinetic properties of free radicals formed in the γ-irradiation of thermally [illegible] various degrees of cross-linkages have been investigated by the EPR method. The thermal vulcanizate was obtained by preliminary heating of the purified polymer in the press at 220C and under 50 t/cm^2 pressures from 5 to 60 hours. The specimen was irradiated in vacuum at -196C from a Co^{60} source of 25 Mrad dose. The EPR spectra of the irradiated specimen were obtained on the EPR-2 IKhF AN SSSR instrument at -196C in 20 to 100° intervals. It is shown that formation of a three-dimensional network prolongs the lifetime of the

Card 1/2

ACCESSION NR: AP4017634

captured radicals. The rate of annihilation of these radicals decreases with increase in the number of cross-linkages. The rate for the same network density is limited by the mobility of the various chain segments. Furthermore, the activation energies and pre-exponential factors for the annihilation of free radicals in "mobile" and "sluggish" regions of the chain have been determined. Orig. art. has: 5 figures and 1 table.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics AN SSSR); Nauchno-issledovatel'skiy institut rezinovoy promy*shlennosti (Scientific Research Institute of the Rubber Industry)

SUBMITTED: 13Nov62 DATE ACQ: 23Mar64 ENCL: 00

SUB CODE: CH NO REF SOV: 005 OTHER: 000

Card 2/2

ACCESSION NR: AP4043774 S/0190/64/006/008/1391/1393

AUTHOR: Goglev, R. S., Neyman, M. B.

TITLE: Thermo-oxidative degradation of polypropylene oxide

SOURCE: Vy*sokomolekulyarny*ye soyedineniya, v. 6, no. 8, 1964, 1391-1393

TOPIC TAGS: oxidation, oxidative degradation, polymer oxidation, polypropylene, polypropylene oxide, propylene oxide, antioxidant

ABSTRACT: The duration of the induction time (τ) of the reaction as a function of temperature, oxygen pressure and the presence of antioxidants was investigated in a study of the oxidative degradation polypropylene oxide, using a method described in an earlier paper. The polymer, with a melting point of 69C and a molecular weight of 40,000, was prepared by catalytic polymerization of propylene oxide in the presence of ferric chloride and purified by repeated precipitation by water from an acetone solution acidified with hydrochloric acid. The effective activation energy for the oxidation of the polymer, found from a curve of lgτ vs. 1/T, is 22 kcal/mol. The induction time was inversely proportional to both temperature and oxygen pressure; yielding hyperbolic curves. Curves showing the retardation of the oxidation by additions of 2,2-methylene-bis-(4-methyl-6-tert.-butyl

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