DOLGOPLASK, B. A., YERUSALIMSKIY, B. L., MILOVSKAYA, E. B., and KOVURENKO, A.P.

"Free radicals and unsaturated compounds in polyerzation," a paper presented at the 9th Congressuon the Chemistry and Physics of High Polymers 30 Jan-2 Feb 57, Moscow, Polymer Research Inst.

B-3,084,395

DOLGOPLASK, B. A., TINYAKOVA, E. Y., REYKH, V. P., and KALAMS, A. E.

"Synthesis of acrylic rubbers and their properties," a paper presented at the 9th Congress on the Chemistry and Physics of High Polymers, 28 Jan-2 Feb 57, Moscow, Rubber Research Inst.

B-3,084,395

DOLGOPLASK, B. A., TINYAKOVA, E. N., and RAMIN, V. P.

"Redox systems in polymirization," a paper presented at the 9th Congress on the Chemistry and Physics of High Polymers, 28 Jan-2 Feb 57, Moscow, Polymer Research Inst.

B-3,084,395

DOLGOPLASK, B. A., NIKOLAYEV, N. Y., and KROPATCHEV, V. A.

"Complex formation and chain structure of some diene polymers," a paper presented at the 9th Congress on the Chemistry and Physics of High Polymers, 28 Jan-2 Feb 57, Moscow, Polymer Research Inst.

B-3,084,395

DOLGOPLOSK, B. A., Institute of Macromolecular Compounds, AS USSR, Leningrad

"Redox Systems in the Initiation of Radical Polymerization, and Their Mechanism of Action," a paper submitted at the International Symposium on Macromolecular Chemistry, Prague, 3-15 Sep 1957.

15 15

Increasing the adhesion of tire cord to rubber. D. A. [illegible]
[illegible] I. A. [illegible], [illegible] I. [illegible] Kuzmak, [illegible]
[illegible] B. [illegible] [illegible]yan[illegible], and S. [illegible] Khokhlovskii. U.S.S.R. 105,[illegible], July [illegible], 1957. To increase the adhesion, the cord is [illegible] with a carboxyl-containing divinylstyrene latex.
M. Howl[illegible]

1-112 2 c (7)

17

Dobrespolsky, B. N.

Oxidation-reduction systems for initiation of radical processes. VI. Hydrogen with participation of oxygen for initiation of the process of oxidative destruction of polymers. B. I. Chayenko, [illegible] A. Dobrospolsky and V. N. Pa[illegible] (Polytechnic Inst., Leningrad). Izvest. Akademii Nauk S.S.S.R., Otdel. Khim. Nauk 1957, 1111-21; cf. C.A. 51, 18[illegible].—Cou[illegible] butadiene rubber and butadiene-styrene rubber samples were used in a study of viscosity changes produced by O attack on the polymers in the presence of Fe(III) naphthenate, with and without S-C_6H_5NHR, with or without activators such as $PhNH_2$, $(PhNH)_2$, di-B-dihydroxyanthraquinone, benzoin, di-tert-butylhydroquinone, trishydroxyphenol, or mercaptobenzothiazole. Kinetic curves for the oxidation of the polymers and those for the action of H_2O_2 on the rubber polymers are shown for the indicated examples. It was shown that in hydrocarbon media these reduction-oxidation systems can be used for effective initiation of radical chain destruction of polymers at room temp. G. M. Kanolopov

Distr: 4E4j/4E3d/4E2c

AUTHORS: Belonovskaya, G. P.; Dolgoplosk, B. A.; Tinyakova, Ye. I. 62-1-9/21

TITLE: Oxidation-Reduction Systems for the Initiation of Radical Processes. Part 2. Initiation of Polymerization in Aqueous Emulsions under the effect of Reversible Systems at a Temperature of below 0° and Study of the Microstructure of the Polymeric Chain (Okislitel'no-vosstanovitel'nye sistemy dlya initsiirovaniya radikal'nykh protsessov. Soobshcheniye 2. Initsiirovaniye polimerizatsii v vodnykh emul'siyakh pod vliyaniyem obratimykh sistem pri temperature nizhe 0° i izucheniye mikrostruktury polimernoy tsepi).

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1957, No. 1, pp. 65-69 (U.S.S.R.)

ABSTRACT: The purpose of this report is to study the applicability of an oxidation-reduction system, consisting of dienols, hydrogen peroxide of isopropylbenzene and very small amount of ferric salt or cupric salt, for the initiation of polymerization in an aqueous emulsion at very low temperatures for the purpose of establishing the relation between the

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62-1-9/21

Oxidation-Reduction Systems for the Initiation of Radical Processes. Part 2. Initiation of Polymerization in Aqueous Emulsions under the effect of Reversible Systems at a Temperature of below 0° and Study of the Microstructure of the Polymeric Chain

polymerization temperature and the microstructure of the polymeric chain. It was found that the application of such system is perfectly possible for polymerization initiation at temperatures ranging down to -47°. It is evident from results obtained that the system containing dicoxymaleic acid and ferric salt is the most active one but only in the presence of hydrogen peroxide of r-tertiary-butyl-isopropyl benzene.

The authors obtained data which established a close relation between the polymerization temperature of Divinyl and isoprene and the microstructure of the polymeric chain. A reduction in polymerization temperature displaces the equilibrium toward a more stable trans-form. Divnyl polymers at a reduced polymerization temperature show a positive tendency toward crystallization.

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Tables, graphs, illustrations. There are 11 references, of which 2 are Slavic.

62-1-9/21

Oxidation-Reduction Systems for the Initiation of Radial Processes. Part 2. Initiation of Polymerization in Aqueous Emulsions under the effect of Reversible Systems at a Temperature of below 0° and Study of the Microstructure of the Polymeric Chain

ASSOCIATION: Academy of Sciences of the USSR, Institute of High Molecular Compounds

PRESENTED BY:

SUBMITTED: December 13, 1955

AVAILABLE: Library of Congress

Card 3/3

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000410810015-1"

Volgoplosk, D. A.

Preparation and properties of synthetic [illegible]

[illegible] Ishizaka, H. [illegible] Takeuchi, I. S. [illegible] Ishizaka and [illegible] Smith. [illegible] (1957) — Isoprene was polymerized with [illegible] et al. (1, 4, 34, 1956) and TiCl4 catalysts [illegible] prepn (10-2) vol.-% in C6H6 was treated [illegible] 0.3-0.6 vol.-%, based on monomer, [illegible] room temp. the temp. rose to 40-60°. The product [illegible] washed with HCl-EtOH and crystd. [illegible] The [illegible] grams of treated rosin polymerized 20 min at [illegible] rollers of 1.5 in. diam. The nitrated spectra showed [illegible] presence of 1.4% 1,4 links, 2-3% 1,2 links and [illegible] 90% 1,4-cis links. The temp. of vitrification varied [illegible] from -67° to -75°. The phys. properties and the [illegible] ability of the polymer were similar to those of natural [illegible] ber.

L. Berman

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000410810015-1"

Oxidation-reduction systems for initiation of radical processes. IV. Oxidation-reduction systems for initiation of polymerization in hydrocarbon media. E. L. Tiuvakina, [illegible] Polymers, Acad. Sci. U.S.S.R., Moscow. [illegible] Polym. S.S.S.R., Otdel. Khim. Nauk 1957 [illegible] 10 of C.A. 51, 7830a — Mechanism of reaction in the system of cumene hydroperoxide or BaO_2 with di-Et dithiocarbamate or benzoin with reduction-oxidation catalys. Fe naphthenate, was examined; kinetic curves of cumene ption of peroxide and that of polymerization of PhCH:CH$_2$ in the presence of the same hydroperoxide and naphthenate of Co, Cu, Pd, Cr, Pb, Ag, Cr, Ni, Fe were given. The metal naphthenates are arranged in descending series as oxidation catalysts: Co, Cu, Pd, Mn, Pb, Ag, Cr, Ni, Fe [illegible] variable valences are quite efficient polymerization catalysts. They effectively [illegible] the [illegible] of the hydroperoxide as shown by kinetic curves of [illegible] in PhCH:CH$_2$ [illegible] the values of the [illegible] the first case H [illegible] are formed, in the [illegible] products: HO [illegible]

DOLGOPLOSK, B.A.

TINYAKOVA, Ye.I.; DOLGOPLOSK, B.A.; REYKH, V.N.

Redox systems for initiating radical processes. Report No. 5: Redox systems for structuring rubber. Izv.AN SSSR.Otd.khim.nauk. no.7:851-857 Jl '57. (MIRA 10:10)

1.Institut vysokomolekulyarnykh soyedineniy AN SSSR.
(Polymerization) (Hydrocarbons)

DOLGOPLOSKIY B.A.

AUTHOR: None Given 3-9-19/31

TITLE: Inter-vuz Scientific Conferences (Mezhvuzovskiye nauchnyye konferentsii)

PERIODICAL: Vestnik Vysshey Shkoly, 1957, # 9, pp 73 - 76 (USSR)

ABSTRACT: In January 1957, the Second All-Union Conference on Photosynthesis took place, organized by the Institute of Plant Physiology of the Academy of Sciences, USSR, and by the Faculty of Soil-Biology of the Moskva University. About 700 representatives of 130 scientific-research institutes, vuzes and ministries were present. The introductory report was made by Academician A.L. Kursanov who described the development of photosynthesis during the last ten years and invited the scientists to concentrate their work on the application of radioactive and stable isotopes. Nearly 100 reports were read: 13 on photochemistry, 9 on the investigation of chloroplast structure, 19 on the investigation of pigments, 9 on the photosynthesis of water plants, bacteria, etc.

Reports on the results reached in the field of photosynthesis were made by: Doctor G. Polster from the German Democratic Republic, Professor N. Seledzhanu from the Rumanian People's Republic, Professor K. Popov from the Bulgarian People's Republic. Finally the Conference stated the great role of Soviet scientists in the development of photosynthesis and gave some defi-

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ciencies in the research organization, in particular, the insufficient participation of biologists in the solution of the problem in question.

The Ninth Conference on High-molecular Combinations took place from 28 January to 1 February. It was organized by the USSR Academy of Sciences and the MGU and concentrated on general matters of polymeric chemistry and physics. About 1500 scientists were present from 172 organizations and 37 towns of the Soviet Union, the representatives of 42 vuzes and 17 foreign scientists from China, East Germany, Poland, Rumania, Czechoslovakia, Yugoslavia, the German Federal Republic and Israel.

The introductory speech was made by Academician V.A. Kargin, who described the present state of science relating to polymers, and invited the scientists to concentrate their work on new methods of obtaining polymers, and new classes of high-molecular substances. In the section of polymeric synthesis 43 papers were read. The author enumerates the following reports: Academician A.N. Nesmeyanov on the reaction of ethylene polymerization and carbon tetrachloride.

S.S. Medvedev, Member-Correspondent of the USSR Academy of Sciences, on the kinetics of various types of polymerization.

Professor B. A. Dolgoploska (Leningrad) on the initiation of radical polymerization.

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A.A. Korotkov (Leningrad) on catalytic polymerization.

V.V. Korshak, Member-Correspondent of the USSR Academy of Sciences (Moscow) on syntheses of phosphor containing polymers.

Professor G.Kh. Kamay (Kazan') on syntheses of certain unsaturated ethers of phosphinous acids.

Academician O. Vikhterle and Professor Vesely (Czechoslovakia) on cation polymerization of olefines.

K.A. Andriyanov, Member-Correspondent of the USSR Academy of Sciences (Moscow) on the elaboration of a new class of thermostable polymers.

Professor Z.A. Rogovin on the qualities of methyl carbonic ether of celluloses.

Professor V.I. Ivanov on cellulose qualities and their application in chromatography.

Professor Van-Yu- Khay (China) on the titration of terminal groups of polycaprolactams.

Academician V.A. Kargin (Moscow) and G.S. Markova on the orientation and crystallization of polymeric chains and their disposition.

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Academician P.A. Rebinder (Moscow) and Professor G.V. Vinogradov on methods characterizing the viscous elastic qualities

of polymeric solutions and the application of new rheological and optical polarization methods.

Professor K. Hess (Gess) from the Federal German Republic, on submicroscopic structures of polymers.

Yu. S. Lazurkina (Moscow) and Ye.V. Kuvshinskiy (Doctors of Physics-Mathematics) on the qualities of polymeric glass and the mechanics of glass formation of high molecular combinations.

Professor Chen-Bao-Kun (China) on viscous plastic qualities of natural rubber.

Professor S. Goreyko (Poland) on polyvinyl chloride qualities.

Professor Z.A. Rogovin on investigations in obtaining fluorine containing synthetic carbon chain fibres.

Professor Kh. Simionesku (Rumania) on fractionation of cellulose.

Professor T. Rabek (Poland) on the qualities of ion-exchange resin.

The second Vuz Conference on Embryology took place from 28th January to 5th February at the Moskva University. About 600 participants were present, and 150 reports were read. Present also were Professor G. Muller (Halle, GDR) and A. Kelyus (Krakow, Poland).

The resolution of the Conference contained recommendations to increase theoretical work on the problems of individual develop-

ment of organisms. The creation of an embryology periodical was suggested.

The Moscow University convened the first Vuz Conference on Biochemical and Physico-chemical Principles of the Biological Action of Radiation in February 1957. About 700 participants were present.

An introductory paper was read by Professor B.N. Tarusov (Moscow) dealing with the biological action of ionizing radiations. Professor A.M. Kuzin made a report on radiotonal biochemical aspects. Other reports were:

Professor M.N. Meysel' (Moscow) on the effect of radiation on various components of the cells of micro-organisms. N.P. Dubinin, Member-Correspondent of the USSR Academy of Sciences (Moscow), on radiation genetics.

The resolution of the conference dealt with the creation of a course in radiation genetics, to be included into the program of genetics and biophysics. The conference decided moreover to invite qualified specialists to investigate the biological action of radiation. It was decided to apply at the Ministry of Higher Education for the organization of courses dealing with working methods of isotopes.

Inter-vuz Scientific Conferences 3-9-19/31

A scientific conference dealing with problems of the structure of organic combinations, took place from 14th to 16th January 1957 at the Kazan' University. More than 200 participants were present and 19 reports were delivered on subjects of theoretical organic chemistry (tautomerism, geometry of organic molecules, etc). The conference stated the successful development of the theory of A.M. Butlerov, and the necessity to resolve problems of modern organic chemistry through physical research methods, such as infrared spectroscopy, spectroscopy of the combined dispersion of light and the methods of magnetic resonance, introduced by Ye.K. Zavoyskiy.

A conference on the Economical Efficiency of New Techniques in Construction was convened in January 1957 by the Moskva Institute of Engineering and Economy, together with the economic departments of Gosstroy SSSR and the Scientific-Technical-Society of the USSR Construction Industry. About 430 participants heard 46 reports. Professor, Doctor of Technical Sciences, L.I. Onishchik (Moscow) spoke on "Problems of Wall Building From the Point of View of Economical Efficiency".

Professor Ye.I. Varonik, Doctor of Technical Sciences (Moscow), spoke on "The Evaluation of the Economical Efficiency of Constructions With Selected Sections".

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Inter-vuz Scientific Conferences

3-9-19/31

V.P. Lagutenko, chief engineer of the Mosgorispolkom Department of Architectural Planning, on "Rational Solutions in the Construction of Buildings - A Principle of Economical Building".

In May 1957 a conference of leading workers of soil division work in USSR was held at the Moskva University.

Representatives of 8 universities and 2 agricultural institutes were present, as well as members of the USSR Academy of Sciences and the Soil Institute imeni Dokuchayeva of the USSR Academy of Sciences.

Eight reports and 3 information papers relating to the principles and situation of soil division in many Soviet areas were read. The conference decided to develop this work, and to apply at the Ministry of Higher Education to convene a conference on this subject in January 1958.

AVAILABLE: Library of Congress

Card 7/7

DOLGOPLOSK, B.A.

AUTHORS: Dolgoplosk, B. A., Panfenova, G. A. 79-11-37/56

TITLE: Reactions of Free Radicals in Solutions (Reaktsii svobodnykh radikalov v rastvorakh). XII. Investigation of the Mechanism of the Inhibiting Action of Polyphenols and Aromatic Amines Upon the Process of an Initiated Polymerization (XII. Issledovaniye mekhanizma ingibiruyushchego deystviya polifenolov i aromaticheskikh aminov na protsess initsiirovannoy polimerizatsii).

PERIODICAL: Zhurnal Obshchey Khimii. 1957, Nr 11, pp. 3063-3087 (USSR)

ABSTRACT: Polyphenols and aromatic amines are widely used as inhibitors in initiated polymerizations and oxidations. In spite of many experiments it was hitherto not possible to determine their effect. Most of the researchers think that the inhibiting action of phenols and aromatic amines is based on their direct reaction with peroxides, hydroperoxides or with the initial active centers which are starting points of the chain-process. It was earlier shown by the authors that the inhibiting action of polyphenols and aromatic amines in the case of a thermal polymerization to the full only becomes effective in the presence of oxygen or metallic salts with variable valency, the polyphenols and aromatic amines being

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Reactions of Free Radicals in Solutions. 79-11-7/26
XII. Investigation of the Mechanism of the Inhibiting Action of Polyphenols and Aromatic Amines Upon the Process of an Initiated Polymerization

converted to quinones. These conclusions may, as the authors found, also be extended to cases of the beginning polymerization of various monomers. The authors investigated the action of hydroquinone, phenyl-β-naphthylamine and diphenylamine upon the polymerization of various mono- and diolefines which were initiated by different exciters. In the absence of oxygen the above-mentioned compounds exert no influence upon the polymerization kinetics. Some reduction of the time is only observed in monomers which form highly active polymeric radicals (vinyl-allylacetate).
There are 5 figures, and 7 references, 3 of which are Slavic.

SUBMITTED: October 22, 1956

AVAILABLE: Library of Congress

Card 2/2

1. Free radicals-Chemical reactions 2. Polyphenols-Chemical reactions 3. Amines-Chemical reactions 4. Polymerization-Effects of inhibitors 5. Inhibitors-Chemical reactions

[illegible] of butadiene containing rubber and study of the structure of polymers and vulcanized rubber. [illegible] Kauch. i Reziny, 1957, 18, No. 1, 11-4. On the basis of these experiments carried out at the Voronezh Neorganicheskii Sint. Kauch. (All-Union Synthetic Rubber Research Inst.) [illegible] polymerized with methacrylic acid, suggestions are made on the nature of the high strength of vulcanized rubber in connection with the peculiarities of structure of the vulcanization net co. There are 7 references. 38[illegible]

1. Vsesoyuznyy nauchno-issledovatel'skiy inst. Sinteticheskogo Kauchuka. (micrs)

DOLGOPLOSK, B.A.; REYKH, V.N.; TINYAKOVA, Ye.I.; KALAUS, A.Ye.; KORYUSHENKO, Z.A.; SLADKEVICH, Ye.G.

Carboxyl-containing rubbers. Report no. 2: Basic qualities of vulcanizates from carboxyl-containing rubbers. Kauch. i rez. 16 no.6:1-6 Je '57. (MIRA 10:10)

1.Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im. S.V. Lebedeva.
(Rubber, Synthetic)
(Vulcanization)

DOLGOPLOSK, B.

"Rubber Which Contains Carboxyl Groups," by Prof B. Dolgoplosk, Doctor of Chemical Sciences, Promyshlenno-Ekonomicheskaya Gazeta, No 18, 10 Feb 57

"More than 30,000 products made of rubber are being manufactured. It is natural that the demand for crude rubber constantly increases.

"The staff of the Leningrad Scientific Research Institute of Synthetic Rubber is trying to aid the industry in the task of developing cheap synthetic rubber which would not be inferior to natural rubber in quality and would even be superior to it as far as some technica characteristics are concerned.

"Investigations which have been conducted establish that introduction into the chair-molecule of a small quantity of carboxyl groups makes it possible to increase the mechanical strength of unfilled rubber by a factor of 10-15. Rubber from crude material of the type mentioned is produced without the use of sulfur; metal oxides are used instead.

"Filled and unfilled rubber derived from crude rubber which contains carboxyl groups exhibits superior mechanical properties and has a high elasticity."

SUM. 1305

DOLGOPLOSK, B.A.

AUTHORS: Yerusalimskiy, B. L.; Dolgoplosk, B. A.; and Kavunenko, A. P.

TITLE: Reactions of Free Radicals in Solutions. Part 9. Dimethyldiphenyltetrazene and tetramethyltetrazene as Sources of Free Radicals with Reaction Center on a Nitrogen Atom (Reaktsii svobodnykh radikalov v rastvorakh. IX. Dimetildifeniltetrazen i tetrametiltetrazen kak istochniki svobodnykh radikalov s reaktsionnym tsentrom na atome azota)

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Vol. 27, No. 1, pp. 267-270 (U.S.S.R.)

ABSTRACT: This report presents for the first time data obtained during the study of free radicals with the reaction center on a nitrogen atom. It was established that RNR type radicals are highly active in reactions leading to the separation of the H-atom from the carbon molecule, additional reactions to the vinyl double bond and are capable of exciting the polymerization process. Using dimethyldiphenyltetrazene as an example, the authors established the monomolecular nature of tetrazene decomposition during heating in a solution. The activation energy of this reaction was calculated from kinetic data by the Arrhenius equation and fixed at 33 kcal/mol. The ability of free radicals with a reaction center

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on a nitrogen atom to excite the polymerization process was verified on a styrene-dimethyldiphenyltetrazene system (See Fig.2). The ability of alkylnitrous radicals to react with saturated and unsaturated hydrocarbons was determined by studying the products of thermal decomposition of tetramethyltetrazene in isopropylbenzene and in alpha-methylstyrene. Tetramethyltetrazene appears to be of high thermal stability; at 130° it decomposes in the solution at a slow rate. The constant of the decomposition rate at 145° in isopropylbenzene at a 0.7 mol% concentration is $0.56 \cdot 10^{-4}$ sec^{-1}. The complete absence of dimethylamine in the products of tetramethyltetrazene decomposition in alpha-methylstyrene indicates that the free dimethylnitrous radicals do not become disproportionated.

One table, 2 graphs. There are seven references, of which 1 is Slavic.

Card 2/3

Reactions of Free Radicals in Solutions. Part 9 492

ASSOCIATION: Academy of Sciences USSR, Institute of High Molecular Compounds (Institut Vysokomolekulyarnykh Soyedineniy Akademii Nauk SSSR)

PRESENTED BY:

SUBMITTED: February 17, 1956

AVAILABLE:

Card 3/3

DOLGOPLOSK, B.A.; KOROTKIN, D.Sh.

Reactions of free radicals in solutions. Part 10: Mechanism of the inhibiting effect of polyphenols and aromatic amines on the process of styrene polymerization. Zhur. ob. khim. 27 no.8:2226-2232 Ag '57. (MLRA 10:9)

(Styrene) (Polymerization)

DOLGOPLOSK, B.A.; KOROTKINA, D.Sh.

Reactions of free radicals in solutions. Part 11: Quinone inhibiting action on the process of thermal polymerization of styrol. Zhur. ob. khim. 27 no.9:2546-2553 S '57. (MIRA 11:3)
(Quinone) (Styrol) (Polymerization)

DOLGOPLOSK, B.A.; PARFENOVA, G.A.

Reaction of free radicals in solutions. Part 13: Mechanism of the quinone inhibition action on the initiated polymerization process. Zhur.ob.khim, 27 no.10:2773-2780 O '57. (MIRA 11:4)
(Quinone) (Chemical reaction--Velocity)
(Polymerization)

Dolgoplosk, B.A.

AUTHORS Kropachev, V.A., Dolgoplosk, B.A., Nikolayev, N.I., 20-3-26/59

TITLE Complex Formation and Chain Structure in the Polymerization of Divinyl by Lithium Butyl.
(Kompleksoobrazovaniye i struktura tsepi pri polimerizatsii divinila litiybutilom - Russian)

PERIODICAL Doklady Akademii Nauk SSSR, 1957, Vol 115, Nr 3, pp 516-517 (U.S.S.R.)

ABSTRACT In a series of papers it was determined that on the occasion of the catalytic polymerization of monolefines and dienes the chain structure is to a great extent determined by the nature of the catalytic complex which takes part in the polymerization. Thus the catalytic initial complex has an immediate relation to every prolongation of the chain. The isolation of the pure lithium organic compounds is rather difficult. On this occasion also complex mixtures of the oxidation products of the metal-organic compounds are formed besides the latter. It was expedient to study the influence of oxygen in order to explain the influence exercised by the mentioned oxidation products on the chain structure on the occasion of the butadien polymerization. The authors proved that, as the title says, on the occasion of the polymerization the introduction of relatively small oxygen quantities into the system leads to an essential increase of the members 1,2 in the polybutadien at the cost of a reduction of the members 1,4. Similar was the influence of alcohol and carbolic acid. This knowledge is of fundamental interest since it points out the necessity of protecting the system against the penetration of oxygen, if divinyl on the occasion of its polymer synthesis con-

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20-3-26/59

Complex Formation and Chain Structure in the Polymerization of Divinyl by Lithium Butyl.

tains a maximum quantity of 1,4 members in the chain. Obviously oxygenated products are developing here which form complexes with lithium-organic compounds. An analogous effect is caused by the dialkylmonosulphides the influence of which was carefully studied by the authors in the absence of oxygen (additions of dimethyl-dipropyl- and di-isopropyl sulphide). The influence of the dialkyl sulphide decreases with the increase of the alkyl radical. The complexes can be represented as $RMe.S\begin{smallmatrix}R'\\R''\end{smallmatrix}$ in a general form. Me is the alkaline metal and R, R' and R" are alkyl radicals. Though also complicated complexes can take part in the polymerization, the influence of the complex-forming additions on the chain structure can be represented according to Ziegler as a consequent metal-organic synthesis, beginning with polymerization. (scheme is given). Since the complex-forming addition is immediately connected with the metal of the metal-organic compound it exercises an influence on the character of the carbon-metal-binding in the course of the entire process of chain formation and thus influences the structure of the polymer. There are 2 tables and 1 Slavic reference.

Card 2/2

ASSOCIATION Institute for Highmolecular Compounds of the A.N. of the U.S.S.R. (Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR)

PRESENTED By Kargin, V. A., Academician, February 27, 1957

SUBMITTED January 29, 1957

AVAILABLE Library of Congress

Dolgoplosk, B. A.

AUTHORS Dolgoplosk, B.A. Romanov L.M., Yerusalimskiy, B.L. and Bogomol'nyy, V.Ya. 20-4-27/60

TITLE The Use of Catalysts based on Magnesium Halogen Alkyls and Titanium Tetrachloride in the Production of Amorphous and Crystalline Polymers from α-Olefins and Dienes (Katalizatory na osnove magniygalogenalkilov i chetyrekhkhloristogo titana dlya sinteza amorfnykh i kristallicheskikh polimerov iz α-olefinov i dienov.)

PERIODICAL Doklady Akademii NaukSSSR, 1957, Vol. 115, Nr 4, pp. 731-733 (USSR)

ABSTRACT The production of polymers from aliphatic compounds of the ethylene series on the basis of polymerization by free radicals is only possible for the first representative of this series, namely ethylene. The interaction of the free radicals with the ethylene homologues leads to the formation of low-molecular products due to the rupture reactions in the first stages of the process. Ziegler and his collaborators used the reaction between organo-aluminum compounds and titanium tetrachloride for initiating the ethylene polymerization. Further investigations in this field furnished the possibilities of initiating the olefin polymerization under formation

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20-4-27/60

The Use of Catalysts based on Magnesium Halogen Alkyls and Titanium Tetrachloride in the Production of Amorphous and Crystalline Polymers from α-Olefins and Dienes

of homogeneously built (isotactic) polymers. Later on organo-aluminum compounds could be replaced by other organometallic derivatives, especially by sodium and lithium compounds. The mechanism of these reactions can for the time being not be considered as established. The reaction between the components of the Ziegler reaction has an oxidizing-reducing character and leads to the formation of titanium derivatives of low valence degrees. Ethane and ethylene develop as by-products in the case of triethylaluminum. Kondyrev and Fomina proved that the reaction between magnesium halogen alkyls and the salts of various metals (Fe, Cu, Co, Ni, Cr, Mo) leads to the formation of:

a) equivalent quantities of a saturated and an unsaturated hydrocarbon which correspond to the alkyl of the oragno-magnesium compound, and

b) of reduced forms of heavy metals. The effectiveness of the system R - MgHal - $TiCl_4$ in the initiation of the polymerization was proved by the authors in the case of ethylene, propylene, styrene and isoprene. The former polymerizes at once without pressure or heating from out-

CARD 2/4

20-4-27/60

The Use of Catalysts based on Magnesium Halogen Alkyls and Titanium Tetrachloride in the Production of Amorphous and Crystalline Polymers from α-Olefins and Dienes

seide. The thus obtained polyethylene possesses $/\eta/ = 2,55$ melting point 130 - 138°C, ultimate strength 335 kg/cm^2 and relative extension 730 %. These indices are analogous to those of polyethylene which is obtained by means of the ordinary Ziegler catalyst. Of great interest are data which were obtained by the authors from the polymerization of propylene. It was proved by the authors that on this occasion in the presence of magnesium chloroethyl and tetrachlorotitanium about the same quantities of an amorphous and a crystalline (isotactic) polymer-form develop. At the same time a fraction was isolated which is insoluble in boiling hexane and whose crystallizability was spectroscopically and X-ray structurally proved. In the case of the polymerization of isoprene various polymer forms were also isolated. The simultaneous production of cis-1,4-polyisoprene and trans-1,4-polyisoprene or of the amorphous and the isotactic polyisoprene directly prove that in the system coexist various catalytic

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The Use of Catalysts based on Magnesium Halogen Alkyls and Titanium Tetrachloride in the Production of Amorphous and Crystalline Polymers from α-Olefins and Dienes

complexes of different types which lead to the formation of a polymer structure characteristic of a certain complex. An experimental part with the usual data follows.

There are 2 Slavic references.

ASSOCIATION: Institute for High-Molecular Compounds AN USSR. (Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR)

PRESENTED: By I.N. Nazarov, Academician, April 25, 1957

SUBMITTED: March 22, 1957.

AVAILABLE: Library of Congress.

CARD 4/4

DOLGOPLOSK, B.A.

KARGIN, V.A.

5(3) P4 PHASE I BOOK EXPLOITATION SOV/1589

Akademiya nauk SSSR.

Khimiya bol'shikh molekul; sbornik statey (Chemistry of Large Molecules; Collection of Articles) Moscow, Izd-vo AN SSSR, 1958. 299 p. (Series: Akademiya nauk SSSR. Nauchno-populyarnaya seriya) 30,000 copies printed.

Compiler: G.V. Sklovskiy; Resp. Ed.: A.V. Topchiyev, Academician; Ed. of Publishing House: V.A. Boyarskiy; Tech. Ed.: I.N. Gneeva.

PURPOSE: This book is intended for a wide circle of readers including those who have had no training in chemistry. It can also serve as a manual for propagandists, teachers, and journalists.

Card 1/8

Chemistry of Large Molecules (Cont.) SOV/1589

COVERAGE: This collection of articles reflects the trend for the future development of the Soviet chemical industry as indicated by the May plenary session of the Central Committee of the Communist Party within the framework of the new Seven Year Plan. These articles were published in newspapers and journals. The authors, scientists and industry workers, developed the theme of accelerated development of the chemical industries, and sciences, with stress on the manufacture of synthetic fibers, plastics, and other materials. Some of the articles were abridged, revised, or enlarged. The articles were selected so as to give an adequate survey of the chemistry and technology of high-molecular-weight compounds and their use in industry, agriculture, and in the manufacture of consumers' goods. Mentioned are raw materials for the production of polymers. This book belongs to the popular-science series of the Academy of Sciences. Similar volumes are intended for future publication. No references are given.

TABLE OF CONTENTS:

Chemistry of Large Molecules (Cont.) SOV/1589

PART II

SYNTHETIC MATERIALS: PLASTICS, FIBERS, RUBBER AND THEIR APPLICATION

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DOLGOPLOSK, B.A.

AUTHORS: Belonovskaya, G. P., Dolgoplosk, B. A., Vasyutina, Zh. D., Kulakova, M. N. 62-1-5/29

TITLE: Redox-Systems for the Starting of Radical Processes (Okislitel'no-vosstanovitel'nyye sistemy dlya initsiirovaniya radikal'nykh protsessov) Report 8: On the Mechanism of Behaviour of a System Containing Ethylene Diamine and Hydroperoxide (Soobshcheniye 8. O mekhanizme deystviya sistemy, soderzhashchey etilendiamin i gidroperoksid).

PERIODICAL: Izvestiya AN SSSR Otdeleniye Khimicheskikh Nauk, 1958, Nr 1, pp 24-34 (USSR)

ABSTRACT: Those oxidation-reduction systems consisting of polyethylene-polyamines, hydrogenperoxides, and salts of iron are very important among the numerous redox systems used at present for the starting of the emulsion process of polymerization. In this paper -as in some former ones- the authors emphasize that this system is effective only in presence of salts of iron, and that their rôle consists of the formation of free radicals. The authors investigate 2 schemes of the function of polyamine systems (references 6,7 and references 6,8). The first presupposes the effect of the concentration of amine and the salts of iron. In the case of the second, however, it

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Redox-Systems for the Starting of Radical Processes. Report 5 62-1-5/29
On the Mechanism of Behaviour of a System Containing Ethylene Diamine and Hydroperoxide

was assumed that the introduction of polymerization is connected with the immediate interaction between amine and hydrogen peroxide in the presence of bivalent iron. The kinetics of the interaction between ethylene diamine and the hydrogen peroxide of isopropylene-benzene was investigated in the aqueous- and hydrocarbon medium in the presence of various quantities of iron salts. Here the lacking of a direct binding between the kinetics of the decomposition of the hydrogen peroxide and the kinetics of polymerization was found. Furthermore it was found that the introduction of the polymerization is not immediately connected with ox.-red. reactions. The entire process occurs only after the complete decomposition of hydrogen peroxide. Finally also the structure of the products produced by the decomposition of hydrogen peroxide was investigated in detail. There are 12 figures, 3 tables, and 18 references, 3 of which are Slavic.

Card 2/2

ASSOCIATION: Institute of High-Molecular Compounds, AS USSR (Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR).

SUBMITTED: November 12, 1956

1. Ethylene diamine-Oxidation-reduction reactions
2. Hydroperoxide-Oxidation-reduction reactions 3. Polymerization

DOLGOPLOSK, B.A.

AUTHORS: Dolgoplosk, B. A., Yerusalimskiy, B. L., 78-3-4-13/32
Tinyakova, Ye. I.

TITLE: Generation of Free Radicals in Solutions and Their Reactions in Model Systems (Generirovaniye svobodnykh radikalov v rastvorakh i ikh reaktsii v model'nykh sistemakh). Report of the Conference on Chemical Sciences of the AS USSR on October 30, 1957 (Doklad na sessii otdeleniya khimicheskikh nauk Akademii nauk SSSR, 30 oktyabrya 1957)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1958, Nr 4, pp. 469-481 (USSR)

ABSTRACT: The present paper gives the final results of the work of the authors with - in the field of oxidation - and reduction initiation of radical processes and the investigation of a number of reactions of free radicals. Corresponding to their action the oxidation and reduction systems are given in 3 groups (Ref. 1): To the first kind belong systems in which the reaction takes place between the reducing agent and the oxidizing agent

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Generation of Free Radicals in Solutions and Their Reactions in Model Systems. Report of the Conference on Chemical Sciences of the AS USSR on October 30, 1957

by forming a radical (see formulae 1,2,3). The detailed description of the first type (system with peroxides) follows. Also systems in which also metal salts with varying valence take part (as oxidizing agents) also belong here. The systems of the second kind are of interest in theoretical and practical respects (second type). Among them is also a system which acts with hydroquinone taking part. This system was utilized industrially (initiation of polymerizations in emulsions). There is still a number of other systems in which the reactions take part between the oxidizing agent and the reducing agent by formation of 2 radicals. Those systems belong to the third kind which have a participation of the diazoamino compounds. 2. Systems with participation of ethylenediamine and polyethylenepolyamine. 3. Systems with participation of sulfur and oxygen (as oxidizing agents). After classification of the systems according to their mechanisms the report deals with the different reactions of alkyl- and heteroradicals with various no-

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62-58-4-13/32

Generation of Free Radicals in Solutions and Their Reactions in Model Systems. Report of the Conference on Chemical Sciences of the AS USSR on October 30, 1957

nomers and polymers on which occasion a break of the bonds C-H, C=C, C - C and S - S is formed.
Finally the part played by the cell in the heat stability of polymers was investigated.
There are 2 tables and 44 references, 40 of which are Soviet.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR (Institute for High-Molecular Compounds, AS USSR)

SUBMITTED: December 23, 1957

AVAILABLE: Library of Congress

1. Chemical conference—Report . 2. Free radicals—Solutions—Reactions 3. Free radicals—Solutions—Generation

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DOLGOPLOSK, B.A.

AUTHOR: None given 62-58-4-30/32

TITLE: Anniversary Session of the Department for Chemical Sciences of the AS USSR on October 30 and 31, 1957, and General Meeting of the Department for Chemical Sciences on December 19 and 20, 1957 (Yubileynaya sessiya otdeleniya khimicheskikh nauk Akademii nauk SSSR ot 30-31 oktyabrya 1957 g. i obshcheye sobraniye otdeleniya khimicheskikh nauk 19-20 dekabrya 1957 g.)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1958, Nr 4, pp. 521 - 524 (USSR)

ABSTRACT: On the occasion of the 40th anniversary of the October Revolution a reunion meeting of the Department for Chemical Sciences of the AS USSR took place. In his opening speech N. N. Semenov pointed out the outstanding succes of the USSR in the field of sciences especially in that of chemistry. Scientific lectures of the sessions were held by the following scientists, as was mentioned already earlier: Knunyants, Member, Academy of Sciences, and A. V. Fokin on the "Nitration of Fluorofines", A. L. Midzhoyan, Member, AS Armenian SSR,

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62-58-4-30/32

Anniversary Session of the Department for Chemical Sciences of the AS USSR on October 30 and 31, 1957, and General Meeting of the Department for Chemical Sciences on December 19 and 20, 1957.

on the "Investigations in the Field of the Synthesis of Physiologically Active Compounds", R. Kh. Freydlina, Doctor of Chemical Sciences, reported on the "Investigation of the Telomerization Reaction and the Reaction of the Synthesis on the Basis of Telomers" (Reference 2). B. A. Dolgoplosk, Doctor of Chemical Sciences, spoke on the "Generation of Free Radicals in Solutions and Their Reactions in Model Systems," A. M. Frumkin, Member of the Academy of Sciences, reported on "Some General Problems of Electrochemical Kinetics and the Theory of Ion Reactions" (Reference 4), A. V. Kiselev, Doctor of Chemical Sciences (Reference 5) spoke on "Some Problems of Adsorption Theory", N. M. Emanuel' (Reference 6), Doctor of Chemical Sciences, reported on "New Problems in the Field of Chain Reactions", V. L. Tal'rose, Candidate of Chemical Sciences, spoke on mass-spectroscopic investigations of ion-and radical reactions, A. P. Rehinder, Member,

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62-58-4-30/32

Anniversary Session of the Department for Chemical Sciences of the AS USSR on October 30 and 31, 1957, and General Meeting of the Department for Chemical Sciences **On** December 19 **and** 20, 1957

Academy of Sciences, drew conclusions with regard to the development of physico-chemical mechanics(Reference 7). I. V. Tananayev, Corresponding Member of the AS USSR, gave new data on the chemistry of some rare elements, D. I. Ryabchikov and others spoke on the "Problems of the Chemistry of Rare Earth Elements"; the final lecture was that of V. A. Sokolov, Doctor of Chemical Sciences, on the "Calorimetric Measurements at High Temperatures".
General Regular Meeting of the Department for Chemistry of the AS USSR (December 19 - 20, 1957): A. I. Brodskiy, Corresponding Member, AS USSR, spoke on the "Investigation of Some Reactions of Peroxides and Peracids of Hydrogen by Means of the Isotopic Method", M. M. Shemyakin, Corresponding Member, AS USSR, spoke on the "Use of N^{15} for the Explanation of the Mechanism of Some Organic Reactions", O. A. Reutov, Doctor of Chemical Sciences, reported on the "Investigation of the

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62-58-4-30/32

Anniversary Session of the Department for Chemical Sciences of the AS USSR on October 30 and 31,1957,and General Meeting of the Department for Chemical Sciences **On** December 19 **and** 20,1957

Electrophil and Homolytical Reactions of the Substitution in the Carbon Atom by Means of the Method of Isotope Exchange",I. P. Alimarin,Corresponding Member,AS USSR, reported on new methods of determination of the division of rare elements using organic derivative sulfuric-,selenic- and telluric acids, V. G. Levich, Doctor of Chemical Sciences, reported on the "Diffusion Kinetics of Heterogenous Chemical Reactions in mobile Liquids".There are 8 references,**all** of which are Soviet.

AVAILABLE: Library of Congress

1. Chemical industry—USSR

Card 4/4

AUTHOR: Dolgoplosk, B. A. SOV/138-58-8-1/11

TITLE: The Problem of Synthesizing Ordinary and Special Rubbers (Problema sinteza kauchukov obshchego i spetsial'nogo naznacheniya)

PERIODICAL: Kauchuk i Rezina, 1958, Nr 8, pp 1 - 11 (USSR)

ABSTRACT: Various methods of synthesising these rubbers are reviewed. Natural rubber has a high degree of elasticity in a large temperature interval. This is explained by the low heat formation in the rubbers during repeated deformation. Rubbers which are based on natural rubber, and which contain no fillers, or small amounts of fillers, have a high degree of mechanical strength. Natural rubber has good technological properties. The structure of the hydrocarbon chains, which ensures maximum elasticity, is discussed. The degree of elasticity of the polymer can be ascertained according to the glass temperature at which the elastic properties of the material disappear (Table 1). Polyethylene is a highly elastic material. Its glass temperature is about -90°C; it is a crystalline product. The elasticity is affected by the introduction of double bonds (as in the case of 1,4-polybutadiene), or by the introduction of alkyl groups (2-ethyl-

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SOV/138-58-8-1/11

The Problem of Synthesizing Ordinary and Special Rubbers

butadiene). It can also be increased by the introduction of oxygen or sulphur. Butadiene, and the two alkyl butadienes with unbranched side chains, are most suitable for preparing highly elastic materials. A homogeneous structure of the chain is absolutely necessary for preparing unfilled rubbers with a high degree of strength. Five different methods for obtaining new structural units in the chain by secondary reactions are discussed. The role of the secondary reactions is defined by the conditions of polymerisation, and also by the nature of the polymerisation initiator, especially during catalytic polymerisation. Investigations by Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka (the Soviet Research Institute for Synthetic Rubber) (VNIISK) on catalytic polymerisation processes, including work on Ziegler catalysts, are reviewed. Heterogeneous catalysts containing chromium, molybdenum and other metal oxides were also investigated. The effect of admixtures on the chain structure during polymerization of isoprene and butadiene when lithium organic compounds are used is tabulated (Table 2). Oxygen and sulphur-

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containing compounds affect the structure and a mechanism of the action of very small amounts of such additives is suggested. Various methods of synthesising the below-mentioned rubbers (by older methods and by using Ziegler catalysts) are reviewed, as well as their structure and properties, and are compared with natural rubber: polyisoprene (Table 3), polybutadiene (Table 4), copolymers of ethylene and α olefins (Table 5) and carboxylated rubbers (Table 6). The industrial importance of rubbers SKS-30A (produced by emulsion polymerisation of a mixture of butadiene or styrene or α-methylstyrene at a temperature of +5°C) and of emulsified polychloroprene is discussed. The second part of the article deals with special rubbers such as frost-resistant rubbers, rubbers which are resistant to benzene, thermostable rubbers (polytetrafluoroethylene (Teflon)), polysiloxanes and rubbers showing high wear resistance (polyurethanes). Finally, the preparation, structure and properties of block- and graft polymers and of butyl rubbers are reviewed. Amongst the new types of latexes, butadiene methylvinylpyridine and a carboxylated butadiene latex are most important for the manufacture of tyre cords. New problems also arise during the stabilisation of

The Problem of Synthesizing Ordinary and Special Rubbers SOV/138-58-8-1/11

rubbers at high temperatures. Aromatic amino-compounds and phenols are unsatisfactory as anti-ageing agents at high temperatures and sometimes even activate oxidation processes. The chemical character of ageing of some new types of polymers differs considerably from the oxidation ageing of ordinary hydrocarbon polymers. There are 6 Tables.

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SOV/ 79-28-6-46/63

AUTHORS: Tinyakova, Ye. I., Khrennikova, Ye. K., Dolgoplosk, B. A.

TITLE: Reactions of Free Radicals in Solution (Reaktsii svobodnykh radikalov v rastvore) XIV. The Formation of Free Radicals in the Decomposition of Hydrogendisulfide and Their Reactions With α- and β-Olefines (XIV. Obrazovaniye svobodnykh radikalov pri raspade dvusernistogo vodoroda i ikh reaktsii s α- i β-olefinami)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 1632-1637 (USSR)

ABSTRACT: The present report deals with the reactivity of the .SH radicals with α- and β-olefines; this is of great interest as they play an important part in the sulfur vulcanization process (Ref 4). Hydrogen disulfide was used as source, so to say, of the .SH radicals; the former easily decomposes into H_2O and S, which proceeds especially intensely in the presence of alkali liquors and other compounds of basic character. This decomposition also takes place equimolecularly in organic solvents, such as xylene, toluene, ethylbenzene, etc.; in this connection it must be noted that in the vulcanization of rubber no formation of hydrogen sulfide was observed. Apparently the decomposition of H_2S_2 takes place according to the chain mechanism through the stage of the .SH- and $.S_2H$ radicals, as is the case with hydrogen peroxide:

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SOV/79-28-6-46/63

Reactions of Free Radicals in Solution. XIV. The Formation of Free Radicals in the Decomposition of Hydrogendisulfide and Their Reactions With α- and β-Olefines

$$HSSH \longrightarrow HS. + .SH$$
$$HS. + HSSH \longrightarrow H_2S + HS_2.$$
$$HS_2. + HS. \longrightarrow H_2S + S_2 \text{ (or } H_2S_2 + S)$$
$$HS_2. + HS. \longrightarrow H_2S + S$$

The radical character of this reaction was proved by the decomposition of the hydrogen disulfide in the presence of an acceptor for free radicals, the nitric oxide. In the case of a heating in ethylbenzene solution at 70° and a simultaneous passage of gaseous NO no formation of H_2S_2 takes place. Earlier it was shown that hydrogen sulfide does not enter reaction with NO on the same conditions. The decomposition of hydrogen disulfide in various olefines, containing external and internal double bonds, was investigated. The relative reactivity of the olefines was determined according to the composition of the final products and according to the amount of the forming hydrogen sulfide (Tables 1 and 2). In the decomposition of hydrogen disulfide in olefines having a double vinyl bond (α-pentene, styrene, isoprene) the formation of H_2S is completely obstructed, which is only partly the case with β-pentene, cyclohexene. The conversion products of H_2S_2 with α- and β-pentenes, and cyclohexenes were separated and characterized, and their mechanism of formation were checked. Concluding it may be stated that the reactivity of the α-olefines with respect to the given radicals is by far higher than that of the β-olfines. There are 1 figure, 2 tables

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Reactions of Free Radicals in Solution. XIV. The Formation of Free Radicals in the Decomposition of Hydrogendisulfide and Their Reactions With α- and β-Olefines

mechanism of formation were checked. Concluding it may be stated that the reactivity of the α-olefines with respect to the given radicals is by far higher than that of the β-olfines. There are 1 figure, 2 tables, and 14 references, 10 of which are Soviet.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR i Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka (Institute of High Molecular Compounds, AS USSR and All-Union Scientific Research Institute of Synthetic Rubber)

SUBMITTED: September 2, 1957

1. Free radicals--Chemical reactions

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AUTHORS: Tinyakova, Ye. I., Karennikova, Ye. K., Dolgoplosk, B. A. SOV/79-28-12-24/41

TITLE: On the Effective Mechanism of the Accelerators in the Process of Sulfur Vulcanization (O mekhanizme deystviya uskoriteley protsessa sernoy vulkanizatsii)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 12, pp 3269-3274 (USSR)

ABSTRACT: To explain the effective mechanism of the accelerators in the vulcanization it was necessary to investigate the composition of the products formed in the reaction with sulfur in various solvents, and to compare them to the composition of the decomposition products of H_2S_2 in the same solvents. For this reason, the reaction of monoethanol amine, ethylene diamine and fructose with sulfur in the pentenes-1 and -2, in cyclohexane, isoprene, α-methyl styrene, styrene, ethyl benzene, and in rubber solution at 130-160° was investigated. This process was characterized according to the formation of H_2S. In the case of the reaction of monoethanol amine with sulfur in the pentenes-1 and -2 all main reaction products were separated

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and characterized. In table 1 the data are mentioned which characterize the formation of H_2S in the reaction of sulfur with the vulcanization accelerators, as well as in the decomposition of H_2S_2 in various solvents. In table 2 the experimental results of the composition of the reaction products of sulfur with monoethanol amine in the solution of pentenes-1 and -2 are mentioned together with the results of the experiments on the decomposition of H_2S_2, which are given for the purpose of comparison. It was shown that the reaction of sulfur with various reducing agents which occur in the sulfur vulcanization as accelerators takes place by way of an intermediate stage of H_2S_2 under the formation of $S^{\bullet}$ and $S_2^{\bullet}$. Based on the investigation of the composition of the products formed in the reaction of sulfur with the vulcanization accelerators and in the decomposition of H_2S_2 in α- and β-olefins, a more detailed information on the mechanism of the occurring sulfur formations in the vulcanization process is obtained, and the part is

On the Effective Mechanism of the Accelerators in the Process of Sulfur Vulcanization SOV/79-28-12-24/41

detected which is played by the accelerators therein. It was shown that the outer double bonds are much more reactive in the reaction with the radicals HS· and HS_2· than the inner ones. At temperatures up to 130° the radicals HS· do not separate hydrogen from the aliphatic hydrocarbon solvents. There are 2 tables and 13 references, 8 of which are Soviet.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR (Institute of High-Molecular Compounds, Academy of Sciences, USSR)

SUBMITTED: November 10, 1957

Card 3/3

AUTHORS: Milovskaya, Ye. B., Yerusalimskiy, B.L., Dolgoplosk, B. A. SOV/20-120-2-31/63

TITLE: The Reactions of Free Radicals in Solutions (Reaktsii svobodnykh radikalov v rastvorakh) The Interaction of Free Radicals With Internal and External Double Bonds (Vzaimodeystviye svobodnykh radikalov s vnutrennimi i vneshnimi dvoynymi svyazyami)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 2, pp. 336-338 (USSR)

ABSTRACT: This paper discusses data which characterize the relative activity of the internal and external double bonds in the reaction of interaction with free radicals. The first part of this paper discusses the interaction of the free methyl radical with hydrocarbons and polymers. The intensity of this interaction was estimated indirectly by comparing the decrease of methane (produced according to the reaction $R.+LH \rightarrow RH+L.$) with the yield of CH_4 when the process takes place in a saturated hydrocarbon. The internal double bond is by far less capable for the addition of free radicals than a double bond of the vinyl type. The investigation of the interaction of free methyl radicals with polymers led to the same conclusion. In swollen polystyrene containing 10% isopropylbenzene the methane

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The Reactions of Free Radicals in Solutions. SOV/20-120-2-31/63
The Interaction of Free Radicals With Internal and External Double Bonds

yield amounts to only 9% of the theoretical value, whereas the yield in pure isopropylbenzene amounts to 49%. Transition to very viscous media leads to a decrease of the rôle of effective radical reactions. The second part of this paper deals with the interaction of the free dimethylcyanomethyl radical with 2-butene. The addition of this radical to an internal double bond is realized only to a very insignificant extent. Under the conditions of the experiments discussed in this paper these radicals have a tendency to recombine. Finally the experimental part is discussed. The authors describe the decomposition of methyl-phenyltriazene in several media and also the products of the decomposition of azoisobutyric acid in 2-butene. There are 2 tables and 4 references, 2 of which are Soviet.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR (Institute of High-Molecular Compounds, AS USSR)

PRESENTED: December 24, 1957, by B. A. Kazanskiy, Member, Academy of Sciences, USSR

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The Reactions of Free Radicals in Solution. SOV/20-120-2-31/63
The Interaction of Free Radicals With Internal and External Double Bonds

SUBMITTED: June 25, 1957

1. Free radicals--Chemical reactions 2. Methyl radicals--Chemical reactions 3. Polymers--Chemical reactions 4. Hydrocarbons --Chemical reactions

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SOV/20-120-4-26/67

AUTHORS: ~~Dolgoplosk, B. A.,~~ Yerusalimskiy, B. L., Milovskaya, Ye. B., Belonovskaya, G. P.

TITLE: The Cell Effect and the Thermal Stability of Polymers (Effekt kletki i termostabil'nost' polimerov)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 4, pp. 783-785 (USSR)

ABSTRACT: A great number of organic substances are known whose thermal stability is much weaker in the solution or melt than in the solid state. The most typical examples are compounds with unstable bindings (peroxides, azo- and diazo-compounds) which begin to decompose only at their melting temperature. At the same time they decompose much quicker in solutions and at a much lower temperature (Table 1). According to the authors' opinion the following experimental results render it possible to relate the mentioned phenomenon to a rapid increase of the cell effect (= reaction of the primary recombination of the free radicals) in viscous and solid media. As was proved already earlier the thermal decomposition of methyl-phenyl triazene in a medium of hydrocarbons leads

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to the formation of methane and methyl-aniline (Ref 5). It is most probable that the latter forms as a result of recombination of the radicals which are released at the moment of decomposition in the "cell". The authors proved that in the case of decomposition of methyl-phenyl triazene in systems of hydrocarbon polymers the methane yield decreases with increasing viscosity of the medium. At the same time it was proved that the yield of the product of primary recombination, namely of the methylaniline increases (Table 2). The above mentioned data give evidence as to a considerable influence of the viscosity of the medium on the efficiency of interaction in the cell. The results obtained render possible the discussion of a possible influence of the state of aggregation on the thermal stability of those substances that contain unstable bindings (Table 1) as well as of the polymers that have a high fusing temperature. The difference in behavior of such compounds in solid state and in solution (or melt) may be explained by means of the particularly important part played by the cell effect in solid state. Polyparaxylylene decomposes only after having been melted (at 425°). In the solution this is the case already at 302°. These polymers

are apparently "overheated"; only after surpassing the temperature of vitrification they undergo a destructive decomposition when the viscosity of the system decreases considerably. Hence we may conclude that the thermal stability of polymers with a high melting temperature displays abrupt jumps in connection with the transition from solid state into an elastic one and from the elastic state into the solution. From the above mentioned it may be concluded that the task of increasing the thermal stability of carbon atom chain polymers in vitrified state consists above all in increasing their melting temperature. A high thermal stability of rubber-like polymers can apparently only be reached by the stability of the skeleton bindings of the main chain. There are 3 tables and 8 references, 2 of which are Soviet.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR (Institute of High-Molecular Compounds AS USSR)

PRESENTED: January 6, 1958, by V. A. Kargin, Member, Academy of Sciences, USSR

The Cell Effect and the Thermal Stability of Polymers SOV/20-120-4-26/67

SUBMITTED: January 4, 1958

1. Polymers--Thermodynamic properties 2. Polymers--Decomposition
3. Polymers--Molecular structure 4. Free radical--Chemical effects

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SOV/20-123-4-30/53

AUTHORS: Dolgoplosk, B. A., Corresponding Member, AS USSR, Kropacheva, Ye. N., Nel'son, K. V.

TITLE: The Cis-Trans-Isomerization of Natural Rubber Under the Effect of Organo-Aluminum Compounds and Titanium Tetrachloride (Tsis-trans-izomerizatsiya natural'nogo kauchuka pod vliyaniyem alyuminiyorganicheskikh soyedineniy i chetyrekhkhloristogo titana)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 4, pp 685 - 687 (USSR)

ABSTRACT: As is known, the catalysts of Ziegler (Tsigler) have recently gained importance in the synthesis of polymers of regular structure, especially of cis-poly-isoprene (Refs 1-4). Previously, the effect of physical and chemical properties of the catalysts have been made responsible for the break of the structure of the chain due to the formation of trans-members. These properties were said to influence the addition character of the monomer (diene) in the course of polymerization. In the present paper it was proved that the regular structure can depend on the isomerization of cis-members to trans-members in a complete polymer chain. This is due to the components used

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The Cis-Trans-Isomerization of Natural Rubber Under the Effect of Organo-Aluminum Compounds and Titanium Tetrachloride SOV/20-123-4-30/53

for stimulating the polymerization process. A short survey of publications (Refs 5,6) is given. The said phenomenon is known in the case of polybutadiene (Ref 7), however, not for natural rubber under similar conditions. The isomerizing effect of the compounds mentioned in the title was investigated in solutions of rolled rubber (NR) in benzene, within sealed glass ampoules in argon. The unsaturated character and the microstructure of the chain of each sample were determined. For the latter infrared spectra according to the method of the last mentioned author, reference 8, were used. Table 1 gives the results obtained. Therefrom it is concluded that the components of the Ziegler catalyst ($TiCl_4$, AlR_3, AlR_2Cl) exert an isomerizing effect on the polymer chain of natural rubber. By the example of $TiCl_4$ it was proved that the number of trans-members increases with the concentration of the isomerizing agent and the longer duration of the action. Figure 1 shows very clearly the isomerization of polyisoprene on absorption bands of infrared radiation which correspond to various contents of cis- and trans-members. This isomerization is accompanied

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by a considerable decrease of the unsaturated character of the polymer. Apparently this depends on: a) Cyclization processes within the chain, b) The additivity of the mentioned compounds to the C=C bond. It is probably preceded by the formation of an unstable complex which can decompose under the formation of initial substances. Triethyl aluminum dichloride causes deeper secondary changes of natural rubber; unsolvable amorphous powders with high melting points are formed. $TiCl_4$ leads to similar results, but only if large amounts are used (100% of the rubber weight). There are 1 figure, 1 table, and 8 references, 3 of which are Soviet.

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im. S. V. Lebedeva (All-Union Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev)

SUBMITTED: August 22, 1958

Card 3/3

BOLDYREVA, I.I.; DOLGOPLOSK, B.A.; KROL', V.A.

Reactions of organometallic compounds with salts of heavy metals. Part 3: Reactions of organoaluminum compounds with titanium halides. Vysokom. soed. 1 no.6:900-906 Je '59. (MIRA 12:10)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka.

(Aluminum organic compounds)
(Titanium halides)

SOV/79-29-2-45/71

AUTHORS: Kropacheva, Ye. N., Dolgoplosk, B. A., Kulakova, M. N.

TITLE: Oxidoreduction Systems as Stimulants in the Radical Processes (Oksilitel'novosstanovitel'nyye sistemy dlya initsiirovaniya radikal'nykh sistem).
IX. Mechanism and Actual Efficiency of Polyamine Systems in the Polymerization Process (IX. Mekhanizm i effektivnost' deystviya poliaminnykh sistem v protsesse polimerizatsii)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 2, pp 565-575 (USSR)

ABSTRACT: Concerning the effective mechanism all known oxidoreduction systems which are applied as stimulants in the radical processes may be divided into two types. The first one, which is the most wide-spread, consists of systems which act under the participation of metals of variable valency. The reaction in these systems always leads to the formation of a radical:

$$Me^{n} + BX \rightarrow Me^{n+1} + B\cdot + X^{-}$$

$$Me^{n+1} + AH \rightarrow Me^{n} + A\cdot + H^{+}$$, where BX denotes the oxidizing and AH the reducing agent. The second type consists of systems in which

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the oxidoreduction reaction leads to the formation of two radicals, e.g.:

$$ROOH + AH \rightarrow RO\cdot + H_2O + A.$$

$$SO_2 + C_6H_2Cl_3SH \rightarrow (\cdot SO_2H) + C_6H_2Cl_3S.$$

In both types of systems the free radicals form directly in the stage of oxidoreduction reaction. The systems in which hydrogen peroxides and polyethylene polyamines participate belong, according to the present investigation, to a new type of system which is characterized by the fact that the oxidoreduction reaction leads to the formation of a new intermediate product which is thermally unstable and decomposes into radicals, i.e. at lower temperature than is the case with hydrogen peroxide. In spite of the fact that polyamine systems are very often employed for the stimulation of polymerization at low temperatures, the mechanism of its actual efficiency has not yet been explained. The detailed results of this investigation of the composition of the reaction products of the corresponding hydrogen oxide with polyamines made it possible to explain

SOV/79-29-2-45/71

Oxidoreduction Systems as Stimulants in the Radical Processes. IX. Mechanism and Actual Efficiency of Polyamine Systems in the Polymerization Process

the mechanism of the main and side reactions. It was shown that it is possible to employ the polyamine systems for producing a highly active polymerization process in emulsions at 5°.- There are 9 figures, 5 tables, and 25 references, 9 of which are Soviet.

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka (All-Union Scientific Research Institute for Synthetic Rubber)

SUBMITTED: December 19, 1957

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5 (3)

AUTHORS: Belonovskaya, G. P., Vasyutina, Zh. D., Dolgoplosk, B. A. SOV/79-29-3-43/61

TITLE: On the Inhibiting Influence of Some Polycyclic Aromatic Compounds Upon the Polymerization Process (Ob ingibiruyushchem vliyanii nekotorykh politsiklicheskikh aromaticheskikh soyedineniy na protsesse polimerizatsii)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 3, pp 955-958 (USSR)

ABSTRACT: The capability of polycyclic hydrocarbons to react with free radicals has been investigated in many papers (Refs 1-7). The present report describes data concerning the capability of some polycyclic compounds to react with the radical CH_3 . , which forms on the thermal decay of methylphenyltriazine, as well as the influence exerted by the same compounds upon the thermal polymerization process of styrene at 100°. Methylphenyltriazine was used as a source of the free methyl radicals. It decays thermally according to the scheme $C_6H_5-N=N-NHCH_3 \longrightarrow C_6H_5NH. + N_2 + CH_3.$ The methyl radical cleaves off the hydrogen from the solvent and forms methane, the yield of which, in the case of the saturated hydrocarbons,

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amounts to 55-60 % (calculated on the theoretical yield), (Ref 8) In the case of the cleavage of methylphenyltriazine in the presence of quinones and various aromatic compounds, their methylation occurs through the radical, which fact causes a corresponding diminution of methane. In this case, the following concurring reactions take place:

$$CH_3^{\bullet} \xrightarrow[AH]{\text{solvent}} CH_4 + A^{\bullet}$$

$$CH_3^{\bullet} \xrightarrow[J]{\text{inhibitor}} CH_3.J^{\bullet} \text{ (weakly active radical).}$$

With one and the same solvent the amount of methane is capable of characterizing the activity of one or the other compound in relation to the methyl radical. The decay of methylphenyltriazine took place at 110° in the solution of a dry, purified gasoline, which was distilled over in the range of 90-110°. The data obtained are shown in the table. They thus characterize the relative activity of various polycyclic aromatic hydrocarbons to the methyl radical. Among the hydrocarbons investigated, dibenzpyrene proved to be the most efficient

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inhibitor in the thermal polymerization process of styrene. There are 1 figure, 1 table, and 9 references, 2 of which are Soviet.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR (Institute of High-molecular Compounds of the Academy of Sciences, USSR)

SUBMITTED: January 16, 1958

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66418

~~5 (3)~~ 5.3831

AUTHORS: Belonovskaya, G. P., Bresler, S. Ye., Dolgoplosk, B. A., Corresponding Member AS USSR, Os'minskaya, A. T., Popov, A. G.

SOV/20-128-6-22/63

TITLE: Inhibition of a Chain Decomposition of Polymers by Destruction of the Structure Homogeneity by Means of the Copolymerization Method

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 6, pp 1179 - 1181 (USSR)

ABSTRACT: If a small quantity of a more readily polymerizable monomer B is added to a monomer A, a polymerization inhibition effect is produced (Ref 1). This effect is caused by the low reactivity of the radical $\sim B^{\cdot}$ at the end of a growing chain with respect to the principal monomer. The introduction of a certain quantity of a less reactive monomer into the monomer B is of no importance to polymerization kinetics. The basic rules, particular to the process of radical polymerization, may appear in the thermal chain decomposition of polymers. It was to be expected that in this kind of destruction the process would be inhibited by introduction of small quantities of components of a different activity into the homopolymer chain. In the case of such a

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decomposition of the homopolymer $\sim A - A - A - A \longrightarrow A + A - A - A\sim$, each elementary act of monomer separation is accompanied by the formation of a free polymer radical of the same type. Subsequently, the authors discuss a case of decomposition of a polymer chain A which also contains B-links. It is assumed that the radicals $\sim A^{\bullet}$ and $\sim B^{\bullet}$ are very different with respect to their reactivity: $\sim A - A - A^{*} - B^{*} - A - A - A\sim \longrightarrow$ chain decomposition. If the radical $\sim B^{\bullet}$ is more reactive, not only the energy released by the addition of A but an additional $(\sim B^{*} - \sim A^{*})$ energy is required to detach a link A^{*}. In this case, decomposition in the stage $.A^{*} - B^{*} - A - A - A\sim$ is retarded. If the radical $\sim B^{\bullet}$ is less reactive than $\sim A^{\bullet}$, chain decomposition is retarded, for the same reasons, in the stage $.B^{*} - A^{*} - A - A - A\sim$. Thus, thermal destruction must be considerably inhibited by the introduction of even a small number of foreign links into the macromolecule of a polymer decomposing in the form of a chain. The inhibition effect will be the higher, the more the said radicals are distinguished by their reactivity. All this is confirmed experimentally. Figure 1 shows that the introduction of even 1.5% of

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the links of methacrylic acid into the polymethyl-methacrylate chain influences the destruction kinetics of the polymer (Curves 1,2). At a methacrylic-acid content of 15% in the copolymer, the destruction rate is only about 1/8 of that of the homopolymer (Fig 1: 1,3). A similar picture is delivered by the methyl-methacrylate copolymer with methyl-methacrylic amide (Fig 1: 5). The increase in thermal stability of the polymers is evidently only connected with the transition from the homopolymer to the copolymer. The addition of vinyl derivatives (Ref 2) for this purpose represents a special case of the above-mentioned phenomenon. There are 3 figures and 4 Soviet references.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR (Institute of High-molecular Compounds of the Academy of Sciences, USSR)

SUBMITTED: July 8, 1959

Card 3/3

KUTSENOK, B.Ye.; TINYAKOVA, Ye.I.; DOLGOPLOSK, B.A.

Interaction between isopropylbenzene hydroperoxide and rongalite, and the use of this reaction for initiating polymerization in acid media. Vysokom.soed. 1 no.12:1830-1839 D '59. (MIRA 13:5)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka.
(Polymerization) (Sodium formaldehyde sulfoxylate)
(Hydroperoxides)

5 (3)

AUTHORS: Kropacheva, Ye. N., Dolgoplosk, B. A., Otten, V. F., Golodova, K. G.

SOV/79-29-6-16/72

TITLE: Synthesis of 1,4-Polyisoprene by Means of Organosodium Compounds and Titanium Tetrachloride (Sintez 1,4-poliizoprena s pomoshch'yu natriyorganicheskikh soyedineniy i chetyrekhkhloristogo titana). Formation of High-melting Polymers in the Catalytic Polymerization of Dienes (Obrazovaniye vysokoplavkikh polimerov pri kataliticheskoy polimerizatsii diyenov)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 6, pp 1853 - 1856 (USSR)

ABSTRACT: In addition to the polymerization syntheses described in the papers of references 1-4 the authors showed that the complexes of the organosodium compound with $TiCl_4$ are also effective in the polymerization of dienes. On the polymerization of isoprene in benzine solution at room temperature in the presence of isoamyl sodium and $TiCl_4$ two polymers were separated in the molar ratio: an elastomer soluble in benzine and an insoluble amorphous powder. The polymerization products of divinyl are also of the same nature. On changing the component ratio of the

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catalytic complex, i.e. on an increased $TiCl_4$ quantity, the yield in the solid polymer rises. At a ratio of 1:3 of the isoamyl sodium to titanium chloride only a solid polymer is formed (Table 1). With increasing temperature, concentration of the catalyst and the monomer, also the reaction rate considerably increases. The insoluble powdery polymers of divinyl and isoprene are also formed in small amounts on their polymerization in benzine alone with $TiCl_4$. The infrared spectrum analysis of the resultant polymers shows that the polyisoprene soluble in benzine contains about 90% of components of the structure 1,4 (Table 2). In this respect the polymers obtained by the authors differ from the polyisoprene which is formed in the presence of sodium and organosodium compounds without titanium chlorides. The resultant powdery polymers are highly heat-resistant. The reactions in the polymers can proceed in two directions: 1) Reactions which involve the formation of condensed six-membered rings in the chain (Scheme). 2) Reactions between the polymeric chains which lead

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Synthesis of 1,4-Polyisoprene by Means of Organosodium Compounds and Titanium Tetrachloride. Formation of High--melting Polymers in the Catalytic Polymerization of Dienes SOV/79-29-6-16/72

to a building-up of ring structures of uncertain nature. The considerable heat-resistance of the polymers synthesized can be explained by their high melting points (Ref 6). Instead of organosodium compounds also the corresponding organo-compounds of potassium, magnesium and aluminum may be used. There are 2 tables and 8 references, 2 of which are Soviet.

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka imeni S. V. Lebedeva (All-Union Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev)

SUBMITTED: June 11, 1958

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5.(3)

AUTHORS: Tinyakova, Ye. I., Dolgoplosk, B. A., Zelenina, T. P. SOV/79-29-7-61/83

TITLE: Redox Systems for the Initiation of Radical Processes (Okislitel'no-vosstanovitel'nyye sistemy dlya initsiirovaniya radikal'nykh protsessov). X. On the Mechanism of the Effect of Redox Systems With the Participation of SO_2 (X. O mekhanizme deystviya okislitel'no-vosstanovitel'nykh sistem s uchastiyem SO_2)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 7, pp 2377 - 2381 (USSR)

ABSTRACT: Sulfur dioxide, by reason of its duality, may be used in redox systems in combination with both oxidizing agents (peroxides, hydroperoxides) and reducing agents (mercaptans, H_2S, and dienols). As was shown by the authors (Refs 1,2) these systems may be used to induce radical reactions in hydrocarbon media (Refs 1,2). In the present paper experimental data is given which makes an interpretation of the mechanism of the effect of the above systems possible. The reaction of isopropylbenzene-hydroperoxide with SO_2 is extremely fast in hydrocarbon

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Redox Systems for the Initiation of Radical Processes. X. On the Mechanism of the Effect of Redox Systems With the Participation of SO_2

SOV/79-29-7-61/83

solutions and causes a rapid gel formation in rubber solutions. This reaction is accompanied by the formation of polysulfone if styrene is used as a solvent. Nitrogen monoxide prevents this process. Analysis of the reaction products obtained with and without NO proved the reaction to proceed via the radicals (SO_3H), which react with the monomer to give sulfonic acid. It was shown previously (Ref 2) that the reaction of trichlorothiophenol with SO_2 produces a vulcanization of rubber at low temperatures. Thus, this reaction leads to the formation of unsaturated polymers. Its mechanism is that of a chain reaction and the reaction proceeds accordingly, and is accompanied by the addition of trichlorothiophenol and SO_2 to the unsaturated polymer chain. NO prevents this process. There are 3 tables and 7 references, 4 of which are Soviet.

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Redox Systems for the Initiation of Radical Processes. X. On the Mechanism of the Effect of Redox Systems With the Participation of SO_2

SOV/79-29-7-61/83

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR (Institute of High-Molecular Compounds of the Academy of Sciences, USSR)

SUBMITTED: June 16, 1958

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5(3) SOV/20-124-3-29/67

AUTHORS: Tinyakova, Ye. I., Dolgoplosk, B. A., Corresponding Member, Academy of Sciences, USSR, ~~Marey, A. I.~~, Al'tshuler, M. Z.

TITLE: The Production of Crystalline 1-4-Transpolybutadiene and -Polyisoprene and the Investigation of Their Properties (Polucheniye kristallicheskikh 1-4-trans-polibutadiyena i poliizoprena i izucheniye ikh svoystv)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 3, pp 595-597 (USSR)

ABSTRACT: A description is given of the production of the symmetric 1-4-transpolymers of butadiene and isoprene by the aid of oxide catalysts, in particular of chromium oxides on aluminium silicate. - Polyisoprene is stable, its infrared spectrum shows that 99% of the polymer chain possesses the 1-4 trans-configuration. The iodine number corresponds with the theory. Due to the uniform structure, the polymer crystallizes, which could be confirmed by the x-ray photograph. This x-ray photograph is analogous to that of natural β-gutta percha. - Polybutadiene is a crystalline-fibrous substance. As it is difficultly soluble it was pressed into a film

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The Production of Crystalline 1-4-Transpolybutadiene and -Polyisoprene and the Investigation of Their Properties

prior to the photographing of its infrared spectrum. The spectrum confirms the 1-4 trans-configuration. A curve of the deformation on repeated intensive heating was plotted. A table gives the density changes brought about by heating. The infrared spectrum of polyisoprene was photographed by K. V. Nel'son, and that of polybutadiene by Ye. I. Pokrovskiy, and the x-ray photographs were made by L. A. Volkova. There are 2 figures, 1 table, and 3 references, 1 of which is Soviet.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR (Institute of High Molecular Compounds of the Academy of Sciences, USSR)
Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im. S. V. Lebedeva
(All-Union Research Institute for Synthetic Caoutchouc imeni S. V. Lebedev)

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5(1) SOV/20-125-5-33/61

AUTHORS: Kutsenok, B. Yo., Kulakova, M. N., Tinyakova, Ye. I., Dolgoplosk, B. A., Corresponding Member, AS USSR

TITLE: Initiation of the Polymerization Process in Emulsions Under the Influence of Isopropyl-benzene-hydroperoxide and SO_2 (Initsiirovaniye protsessa polimerizatsii v emul'siyakh pod vliyaniyem gidroperekisi izopropilbenzola i SO_2)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 5, pp 1073-1076 (USSR)

ABSTRACT: It was proved already earlier (Ref 1) that the reaction between the substances mentioned last in the title proceeds rapidly in hydrocarbon media. It leads to the formation of unsaturated polymers or to the formation of polysulfone if it proceeds in a styrene solution at SO_2 excess (Ref 2). Therefrom it may be assumed that the reaction of hydroperoxide and SO_2 proceeds through an intermediate stage of the free radicals, in analogy to many other known redox reactions. The present paper deals with the investigation of the effective

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Initiation of the Polymerization Process in Emulsions SOV/20-125-5-33/61
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mechanism of this reaction system as well as with the clarification of its possibility of use for initiating the polymerization of monomers in aqueous emulsions and acid media at low temperature. Investigation of the composition of the interaction products of isopropyl-benzene-hydroperoxide with SO_2. The process mentioned proceeds instantaneously in an octane-water emulsion between 0 - 70°. SO_2 and hydroperoxide are consumed in equimolar quantities (Table 1). If the reaction proceeds in the presence of α-pentene or α-methyl-styrene, which are known to affiliate easily free radicals (Refs 3, 4), sulfo acids are detected in the interaction products (Table 2), Therefore the radical SO_3H forms one of the intermediate products of the reaction. The formation of sulfuric acid as a final product of the oxidation may be due to the reaction of the disproportionation of the radicals. If the acceptors of free radicals lack, the reaction proceeds readily in the direction of the formation

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Initiation of the Polymerization Process in Emulsions SOV/20-125-5-33/61
Under the Influence of Isopropyl-benzene-hydroperoxide and SO_2

of sulfuric acid and carbinol. Initiation of the polymerization under the influence of hydroperoxide and SO_2. Since the interaction of the components in aqueous emulsions and in a homogeneous medium proceeds rapidly, the first experiments of the aforesaid initiation do not yield positive results. The high concentration of active centers at the beginning of the process caused short reaction chains and the end of polymerization. It is known that such systems may be used for initiating the polymerization only by regulating the rate of interaction of the components by different methods. This is achieved especially at 0° with a gradual dosage of the components. Figure 1 shows the yields of the polymer in the presence of 0.6 % of the hydroperoxide mentioned (computed with respect to the styrene weight) and at an equivalent quantity of 0.1 N SO_2-solution according to the sequence of the addition of the components. This shows that with the addition of hydroperoxide and SO_2 the polymerization ceases instantaneously

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Initiation of the Polymerization Process in Emulsions SOV/20-125-5-33/61
Under the Influence of Isopropyl-benzene-hydroperoxide and SO_2

(at the beginning of the reaction) (Curve 1). The process is quickest at a gradual dosage of the two components. The yield amounts here to 87 % at 0° within 4 hours (Curve 2). Figure 2 shows the kinetic polymerization curves of styrene in the presence of various quantities of hydroperoxide. Above 0.3 % and more of the concentration of the latter the polymerization ceases practically. A complete consumption of hydroperoxide and SO_2 corresponds to this moment. The polymerization begins again at a temperature rise up to 30° (Fig 3). Therefore an intermediate compound is produced under certain conditions which is able to initiate the polymerization at higher temperatures. There are 3 figures, 2 tables, and 8 references, 4 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy institut sintaticheskogo kauchuka im. S. V. Lebedeva (Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev)

SUBMITTED: January 5, 1959

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66483

SOV/20-129-1-29/64

~~5(2,3)~~ 5.3831

AUTHORS: Belonovskaya, G. P., Dolgoplosk, B. A., Corresponding Member, AS USSR, Chernova, Zh. D.

TITLE: Investigation of the Reaction of the Oxidation of $TiCl_3$ With Hydroperoxide of Isopropylbenzene in Aqueous and Hydrocarbon Media

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 1, pp 105 - 108 (USSR)

ABSTRACT: Oxidating chain processes are expected to take place in polymers containing Ti^{3+} because of its oxidation to Ti^{4+}; above all, destruction or construction of polymers may be expected. Hence it was attempted to investigate this oxidation and its occurrence without secondary processes which deteriorate the structure and properties of the polymers. The oxidation mentioned in the title was investigated in aqueous solutions and hydrocarbons. Figure 1 shows the interaction of $TiCl_3$ with the above hydroperoxide in aqueous and aqueous-alcoholic solution with and without nitrile of acrylic acid at 20^0 and 0^0, respectively. The ratio of $TiCl_3$ used per 1 mol hydroperoxide is 1:2; in the presence of the acceptor of free radicals (nitrile of

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Investigation of the Reaction of the Oxidation of $TiCl_3$ With Hydroperoxide of Isopropylbenzene in Aqueous and Hydrocarbon Media SOV/20-129-1-29/64

acrylic acid, methylmethacrylate) it is almost 1:1. Reaction takes place also at low temperatures and does not stop until -70°. If the acceptor mentioned is absent, 15-17% of methane (with regard to hydroperoxide) is liberated at 20° in the case of 1% hydroperoxide solution. With a ratio of $TiCl_3$:hydroperoxide = 2:1 at 20° the main products of hydroperoxide decomposition are: dimethylphenylcarbinol (65-75% yield) and acetophenone (15-17%). If it is allowed to stand, TiO_2 is quantitatively separated from aqueous solution. On account of the above data the authors assume that the processes (1)-(4) take place in aqueous solutions (see Diagram). The reactions (2) and (3) are repressed in the presence of the above acceptor. The reaction mentioned in the title can be used for introducing polymerization in emulsion media at temperatures to -50°. Moreover, it can be used for homogeneous polymerization of partially water-soluble monomers (nitrile of acrylic acid, methylmethacrylate) at low temperatures. These substances react in a hydrocarbon medium (benzene with 8-10% absolute ethanol) in a ratio close to 1:1. Since reaction (2) seems to be specific for radicals of the type RO· (HO·) only, it cannot be used in hydrocarbon media for the introduction of processes with great chain length.

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Investigation of the Reaction of the Oxidation of $TiCl_3$ With Hydroperoxide of Isopropylbenzene in Aqueous and Hydrocarbon Media SOV/20-129-1-29/64

The system $TiCl_3$-hydroperoxide is very effective for processes with short chains (e.g. construction of rubber). Table 2 shows the inhibition of polybutadiene and polyisoprene construction by benzoquinone, nitrobenzene, dinitrobenzene, and neozone-D (phenyl-β-naphthylamine). The above results show that the oxidation of Ti^{3+} salts takes place by means of hydroperoxide involved in chain radical reactions The latter can introduce the polymerization process in aqueous media. They lead to rubber construction in hydrocarbon media. These processes can be repressed by specific inhibitors; at the same time, secondary radical processes can be eliminated. There are 1 figure, 2 tables, and 5 Soviet references.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR (Institute of High-molecular Compounds of the Academy of Sciences, USSR)

SUBMITTED: July 10, 1959

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5.3831

~~5(3)~~

67919

SOV/20-129-5-29/64

AUTHORS: Tinyakova, Ye. I., Dolgoplosk, B. A., Corresponding Member, AS USSR, Zhuravleva, T. G., Kovalevskaya, B. N., Kuren'gina, T. N.

TITLE: Polymerization of Dienes and Olefins Under the Action of Cobalt Oxides and Diethyl Aluminum Halides, and a Study of the Structure of Polymers

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 5, pp 1068 - 1070 (USSR)

ABSTRACT: The authors supply data concerning the polymerization of dienes: butadiene, isoprene, pentadiene-1-3, and 2-3-dimethyl butadiene-1-3, as well as olefins: α-butene, styrene and α-methyl styrene in the presence of cobalt oxides (Co_2O_3-Co_3O_4, Ref 6), and diethyl aluminum chloride or diethyl aluminum bromide. The catalyst contained either 71-73% or 6.7% of Co. The latter content refers to cobalt oxide on aluminosilicate. Polymerization was carried out between 0 and 40° in different ratios between cobalt oxide and diethyl aluminum halide (concentration 0.5-2.5 of weight per

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Polymerization of Dienes and Olefins Under the Action of Cobalt Oxides and Diethyl Aluminum Halides, and a Study of the Structure of Polymers

cent referred to the monomer). Oxygen and humidity were kept off. In the polymers produced the content of 1-2-, 3-4- and 1-4-cis- and trans-members was determined by IR-spectroscopic measurement (spectra taken by N. V. Mikhaylova). The unsaturation was determined on the basis of the reaction with iodine chloride (Ref 7). The vitrification temperature was determined according to A. I. Marey (Ref 8). Table 1 gives the results along with the molecular weight. Under mentioned conditions butadiene is rapidly polymerized already at 0°. Cobalt oxide on aluminosilicate retards polymerization to some extent. The polymers obtained exhibit a degree of unsaturation which is 97.5-99% of theory. This points to the absence of secondary reactions with the double bonds of the polymer. Butadiene polymers have a fairly regular microstructure. On cobalt oxide without carrier the amount of the 1-2-members was 5-8%, the total amount of the 1-4-members was 95-92%, with the most part being in the 1-4-cis-position. By the use of cobalt oxide on

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