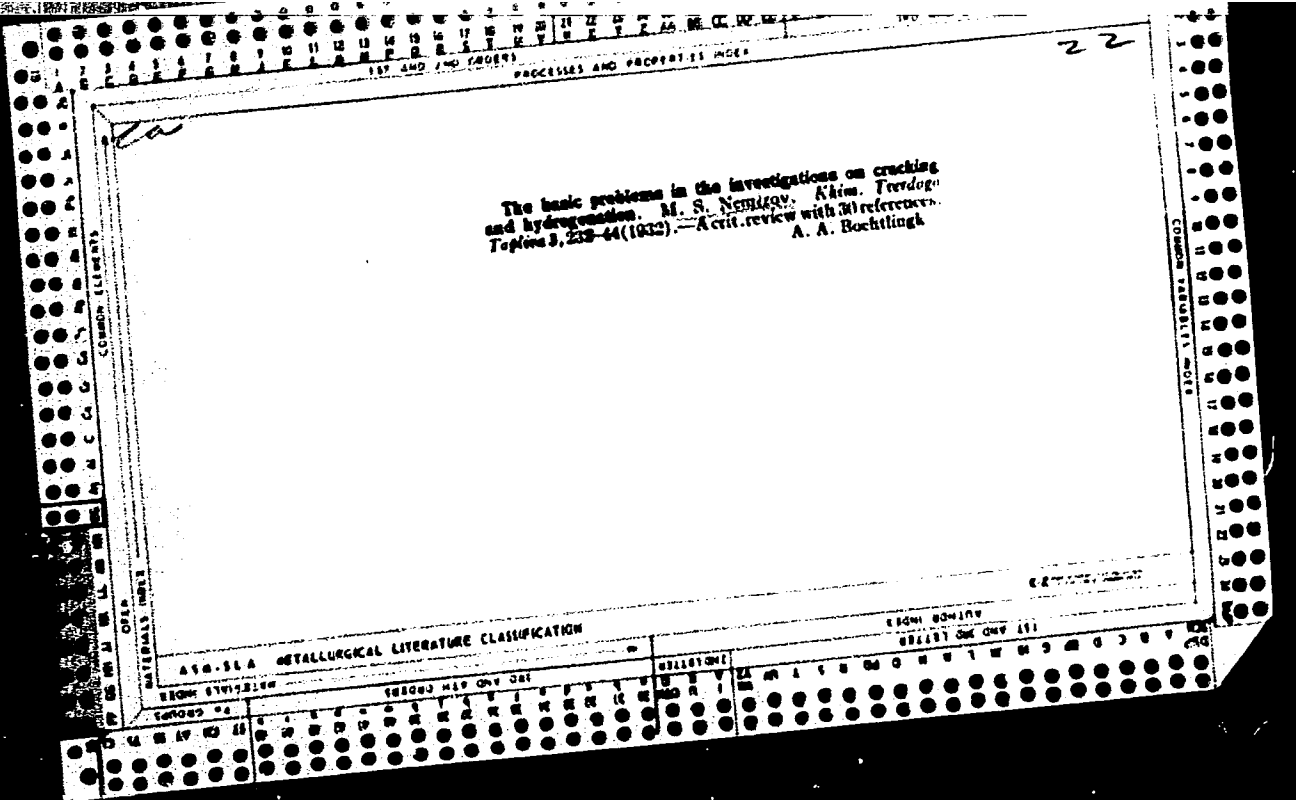
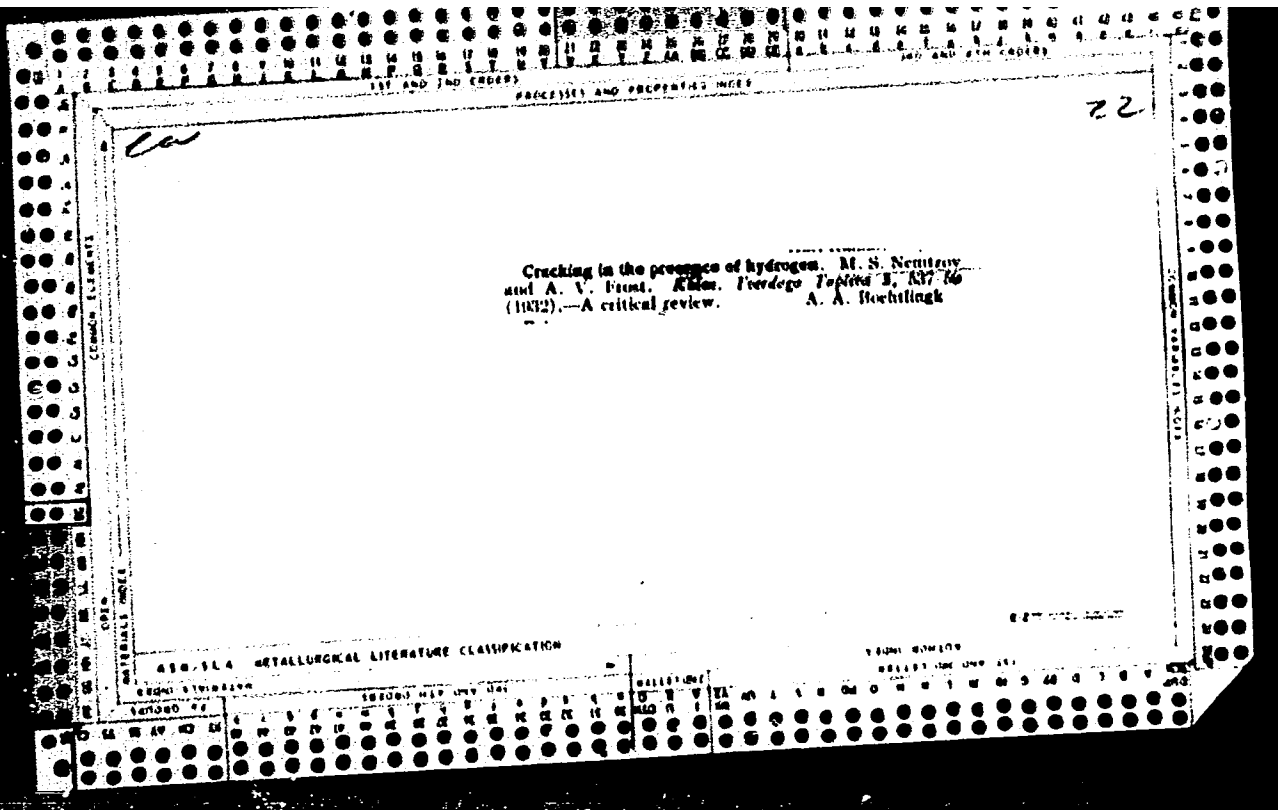


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382





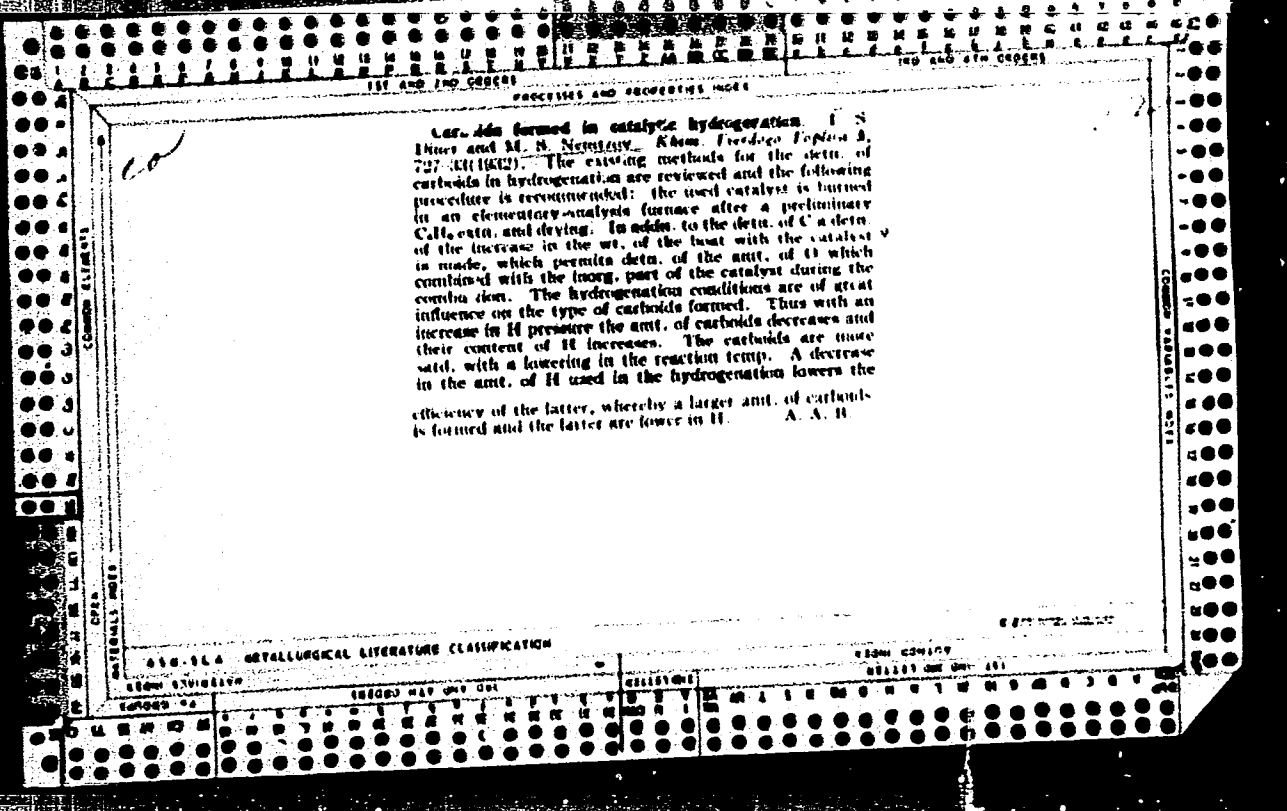
22

Polymerization of olefins from cracked gases. V. N. Spat'ev and M. S. Neumayr, *Khim. Tverdogo Topliva* 5, 707-13(1932).--It was attempted to convert the olefin hydrocarbons (mainly ethylene and propylene) into liquid hydrocarbons of the gasoline type by means of polymerization, and to investigate the polymerization of olefins under conditions similar to those of liquid-phase cracking and cracking in the presence of H_2 . The presence of H_2 in the gas mixt. interferes with a thorough condensation of the olefins and the major portion of the product boils below 300° . In expts. carried out with a synthetic mixt. of H_2 and ethylene, it was found that the polymerization reaction is accompanied by hydrogenation according to: $C_2H_4 + H_2 = C_2H_6$. The latter reaction prevailed to such an extent that in the presence of an excess of H_2 a liquid product was not obtained. Moreover, the walls of the bomb became covered with a layer of C, indicating a cracking of the ethylene or of products of its polymerization. The yield of condensate was considerably increased after leaving the C deposit on the walls of the bomb and carrying out the expts. in a bomb thus covered with C. The gas used contained: H_2 19.6, olefins (among them C_2H_4 3.3% and higher homologs 0.5%) 19.7, CH_4 51.2 and C_2H_6 7.5%. There is no condensation below 350° , while hydrogenation is observed at considerably lower temps. An increase in the temp. favors the hydrogenation velocity as well as the formation of liquid hydrocarbons.

Above 440° , simultaneously with the formation of C_{11} , occurs also a deeper cracking accompanied by the formation of C pptg. on the walls of the bomb. The theoretical part of the reaction is discussed in detail. The theoretical catalyst investigated activated C and Al_2O_3 were of no use. In the presence of fuller's earth it was possible to lower the pressure without lowering the yield of condensate, although the catalyst was rendered inactive very rapidly. The condensate obtained contained 75% of a gasoline fraction which was characterized by a high content of aromatics. The best reaction conditions were a temp. in excess of 400° , H_2 pressure of 300 atm. and slow passage of the raw material through the reaction zone.

A. A. Bochtling

ASB-51A METALLURGICAL LITERATURE CLASSIFICATION



157 AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

22

CA

Destructive hydrogenation in the presence of catalysts. I. J. S. Dine and M. S. Newman. *Khin. Tsvetop. Topika* 8, 827-87 (1928). Hydrogenation expts. were conducted with a Cranny mixed-Cas fuel oil of the following characteristics for the purpose of detg. the variations caused by changing the amt. of stock charged into the autoclave, the velocity of agitation, the severity of the processing conditions and the temp.: flash point 121°, sp. gr. 0.906, pour point 35°, E_v viscosity 4.08, paraffin 10, resins 18 and fraction b. 300° 0%. NiO was used as catalyst at 420-480°. A theoretical analysis of the process is presented and the relationships of thermal decompos.

condensation and hydrogenation are discussed. The energy of activation of the thermal decompos. of the mixt. amounted to 38,000-79,000 cal. II. *Ibid.* 6, 128-31 (1928).—A Ni catalyst which was preliminarily reduced and NiO charged directly into the autoclave give identical results in high-pressure hydrogenation. Increase in the amt. of catalyst up to 20% acts favorably. Coke formation under the above conditions ceases in the presence of 5-8% of the catalyst. The small amt. of carbonaceous formed on the catalyst is stabilized, and no addnl. formation is observed. Increase of the partial H pressure causes a stabilization of the hydrogenation that is reflected mainly in the degree of the aromatization of the products of hydrogenation. The content of aromatic hydrocarbons in the light fractions probably is not in excess of the aqul. concn. The influence of the H pressure on the content of unsatd. compds. is of a kinetic nature, because their concn. is a function of the sp. velocities of the thermal decompos. and the hydrogenation. The unsatd. compds. are the coke-forming agents. Therefore, the elimination of coke formation is governed by the velocity of the reaction. Conclusion: Destructive hydrogenation can be carried

(over)

400-554 METALLURGICAL LITERATURE CLASSIFICATION

ECONOMY ECONOMY

ECONOMY ECONOMY

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50

EST. AND IMP. DIVISIONS PROCESSES AND PROPERTIES INDEX IMP. AND ATN. DIVISIONS

ca

**The influence of pressure in the process of creating.
M. B. Mamantov. *Nefyanye Krasnoto* 23, No. 10, 41-6
(1953).—A discussion based on an extensive study of the
literature (with 44 references) and experiments carried out in
the Government High-Pressure Institute in Petrograd.
A. A. Bocklinsk**

28

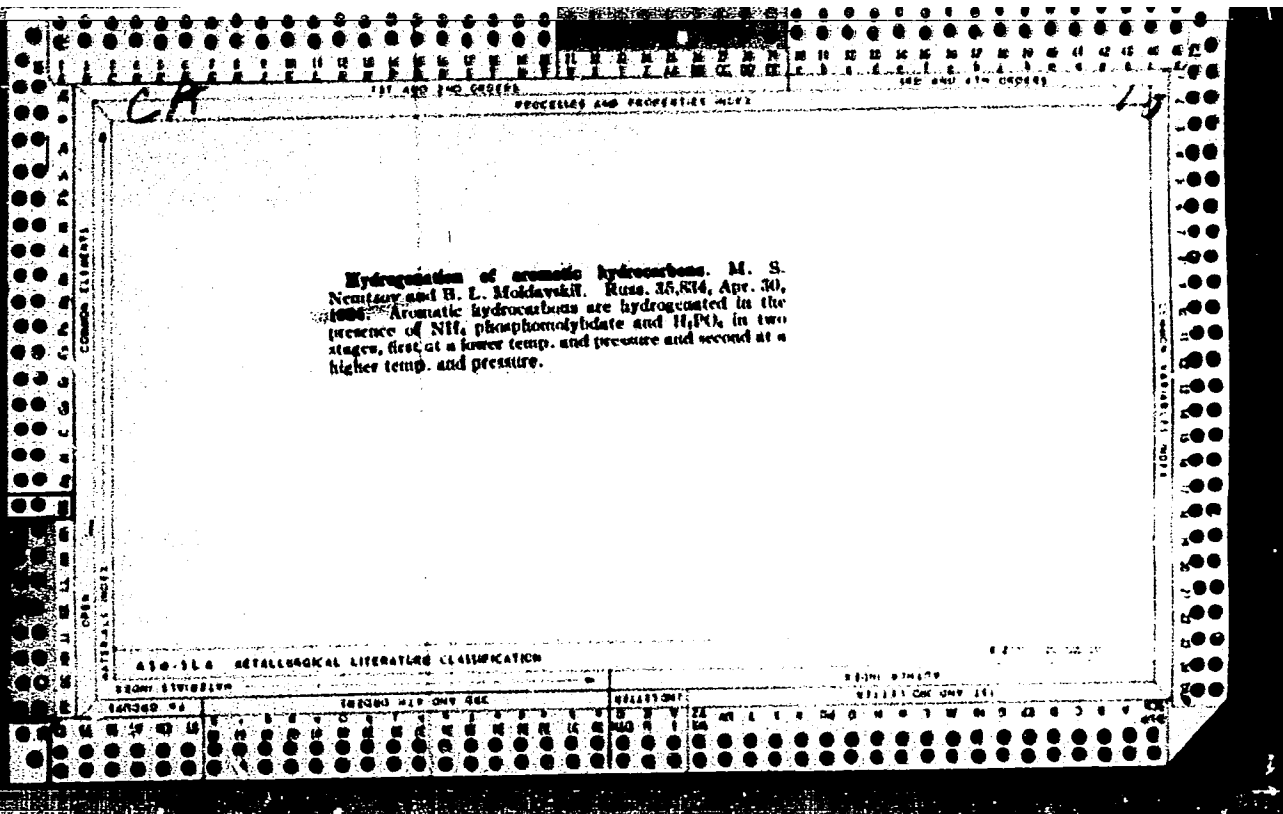
OPEN
CATION ELEMENTS
NATURAL ISOTOPES

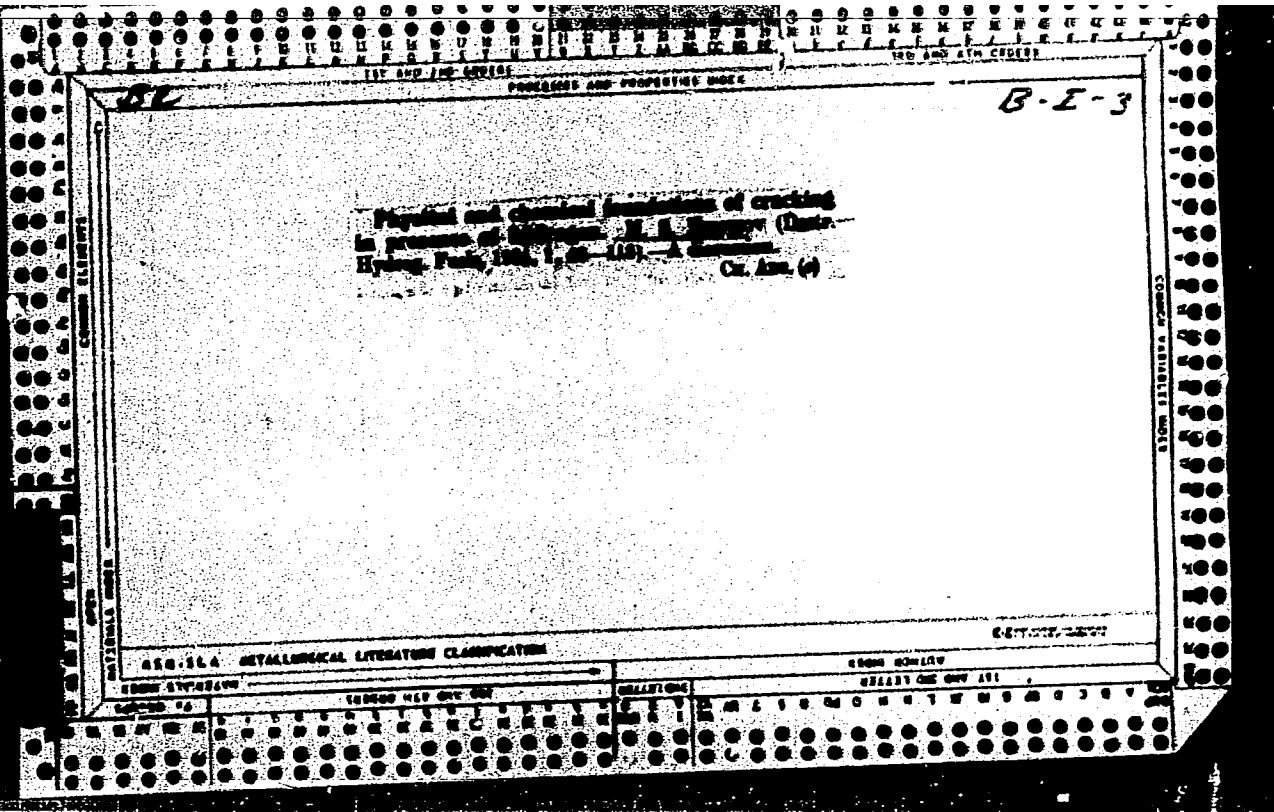
ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

REGION DIVISIONS YEAR DIVISION

SEARCHED SERIALIZED INDEXED

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50





PROCESS AND PROPERTIES INDEX

21

Destructive hydrogenation in the presence of catalysts.
 M. S. Nemtsev. *Destructive Hydrogenation of Fuels*.
 U.S.S.R. I. I. Gokhenshchikov (Leningrad) 4, 110-41
 (1964).—As catalysts for hydrogenation were used MoO_3 ,
 $MoO_3 + H_2BO_3$, $MoO_3 + Cr_2O_3$, $MoO_3 + B$, MoO_3 , spent
 MoO_3 , FeS , $MoO_3 + FeS$ (coarse grain), $MoO_3 + FeS$
 (fine grain), $MoO_3 + FeS + H_2BO_3$, $(NH_4)_2MoO_4 \cdot$
 $4H_2O$, NiO and $(NH_4)_2MoO_4$. The following products
 were subjected to hydrogenation under different condi-
 tions: Crassy paraffinic fuel oil "G," paraffinic distillate,
 naphthalene, tetralin, a mixture of tetralin and decalin,
 xylene, anthracene, cracked residue from the Winkler-
 Koch cracking unit, cracked residue from the Jenkin-
 Koch cracking unit, shale tar and prut tar. The hydrogenation
 products were analyzed in detail. Sixty-two references.
 A. A. Rohtling

METALLURGICAL LITERATURE CLASSIFICATION

FROM SOURCE

CLASSIFY ONE ONLY

117 AND 118 INDEX

PROCESSES AND PROPERTIES INDEX

II. Kinetics
 Catalysts for destructive hydrogenation. On molybdenum
 the hydrogenation of hydrocarbons on molybdenum
 catalysts. L. Altman and M. Nemtsov. *Ann. Physika-*
chem. U. S. S. R. 423-427(1924)(in German); *J.*
Phys. Chem. (U. S. S. R.) 6, 231-237(1933)(in Russian);
J. C. A. 28, 4728. The hydrogenation of PhMe on
 MoS₂ contg. several % MoS₂ from 400° to 600° is in
 order with respect to H₂ and almost zero with respect to
 PhMe. The energy of activation is 23,100 cal. and the
 velocity is given by $\log K = 0.87 + \log [P_{H_2} \times (273/T)]$
 - 22150/T, in which K = g. toluene converted per kg.
 MoS₂ per min. The relative ratios of hydrogenation of
 aromatic compds. increase in the order C₆H₆, C₆H₅Me,
 C₆H₄Me₂, PhMe, C₆H₅Me. At 400-500° MoS₂ is at least
 10 times as active a catalyst as Pt or other metallic cata-
 lysts. Adsorption of hydrocarbons on MoS₂ is assumed to
 be strong in the temp. range used. F. H. Rathmann

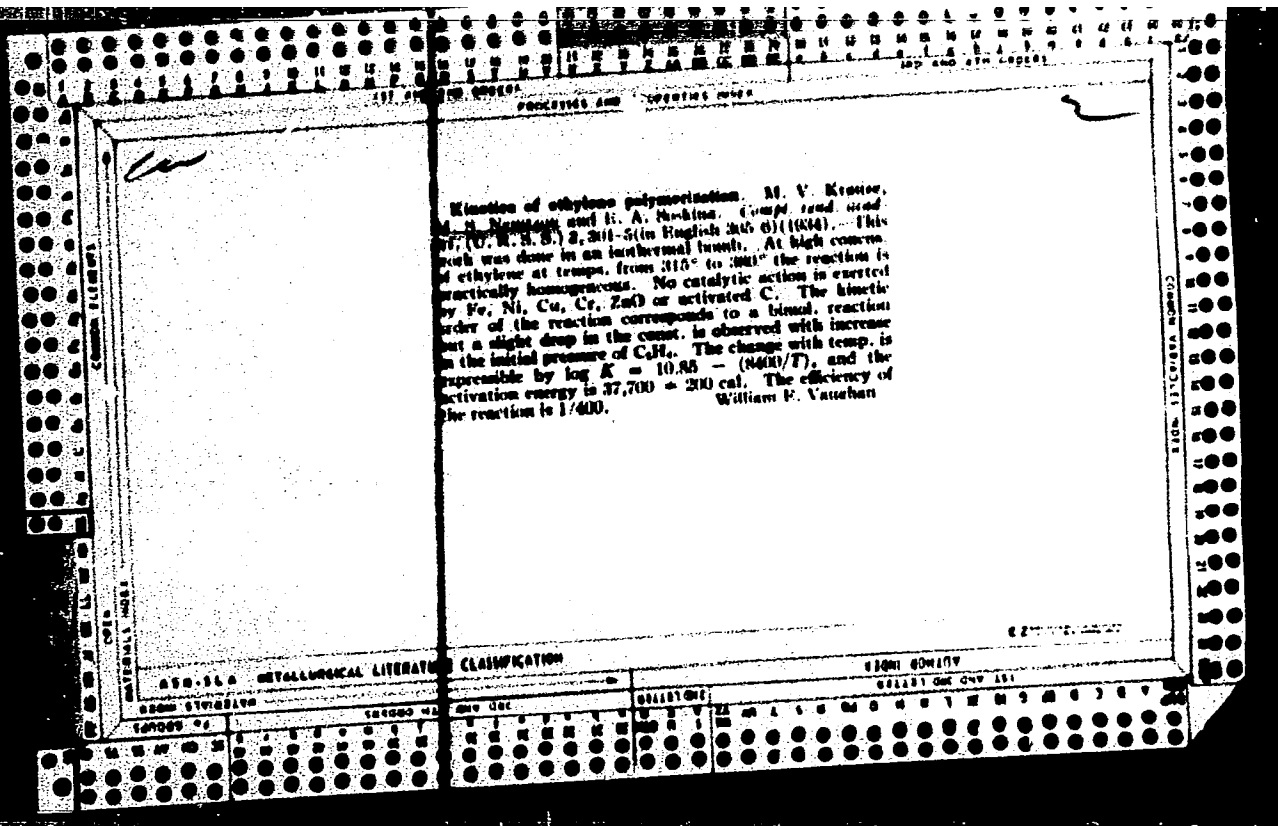
7

ASS-51A METALLURGICAL LITERATURE CLASSIFICATION

SEARCH ONE ONE ALL

SEARCH ONE ONE ALL

SEARCH ONE ONE ALL



10

PROCEEDS AND PROCEEDING NOTES

The polymerization of olefins. Kinetics of the thermal polymerization of propylene, isobutylene and styrene. M. V. Kovacs, M. J. Maguire and R. A. Collins. *Canad. Jour. Chem.* 37, 2735-2742 (1959); *J. Polym. Sci. A-1*, 17, 1009-1017 (1959). The kinetic properties (I), isobutylene (II) and styrene (III) were obtained from the corresponding olef. by Spitzer's method. Pseudo-butylene (IV) was made from butadiene (*J. C. A.* 54, 1957). II contained 94% of normal butyrene and IV contained 2.5% of butyrene. III was a fraction of the dehydration product of fermentation *in-AerOxi*, of unknown structure, b. 27-35°. The samples were sealed into thick-walled glass tubes that were placed (3 at a time) in an isothermal bath. Constant pressure was set up inside the bath by R or benzene. A series of expts. carried out with the above hydrocarbons with varying initial concns. showed that the reaction velocity varies directly as the square of the concn. Expts. at varying concns. with 20-30% conversion showed the dependence of the polymerization velocity const. on temp. The tabulated results demonstrate that the polymerization of olefins at high initial concn. is homo-geneous; that although the mechanism of the reaction differs from the usual consecutive bimol. reaction, the first kinetic order is formally observed; the polymerization reaction velocity of olefins of normal structure rapidly decreases with increase in mol. wt.; the existence of 2 chains to the double bonds increases the velocity of thermal polymerization; the activation energy for polymerization of olefins of normal structure does not apparently change with an increase in mol. wt.; the existence of single chains to the double bonds does not appreciably alter the energy characteristics of the reaction; and finally the existence of 2 chains to 1 of the C atoms of the double bond changes, seemingly, the energy characteristics of the olefin grouping and leads to an increase in the activation energy of the polymerization reaction. C. R. Adkins

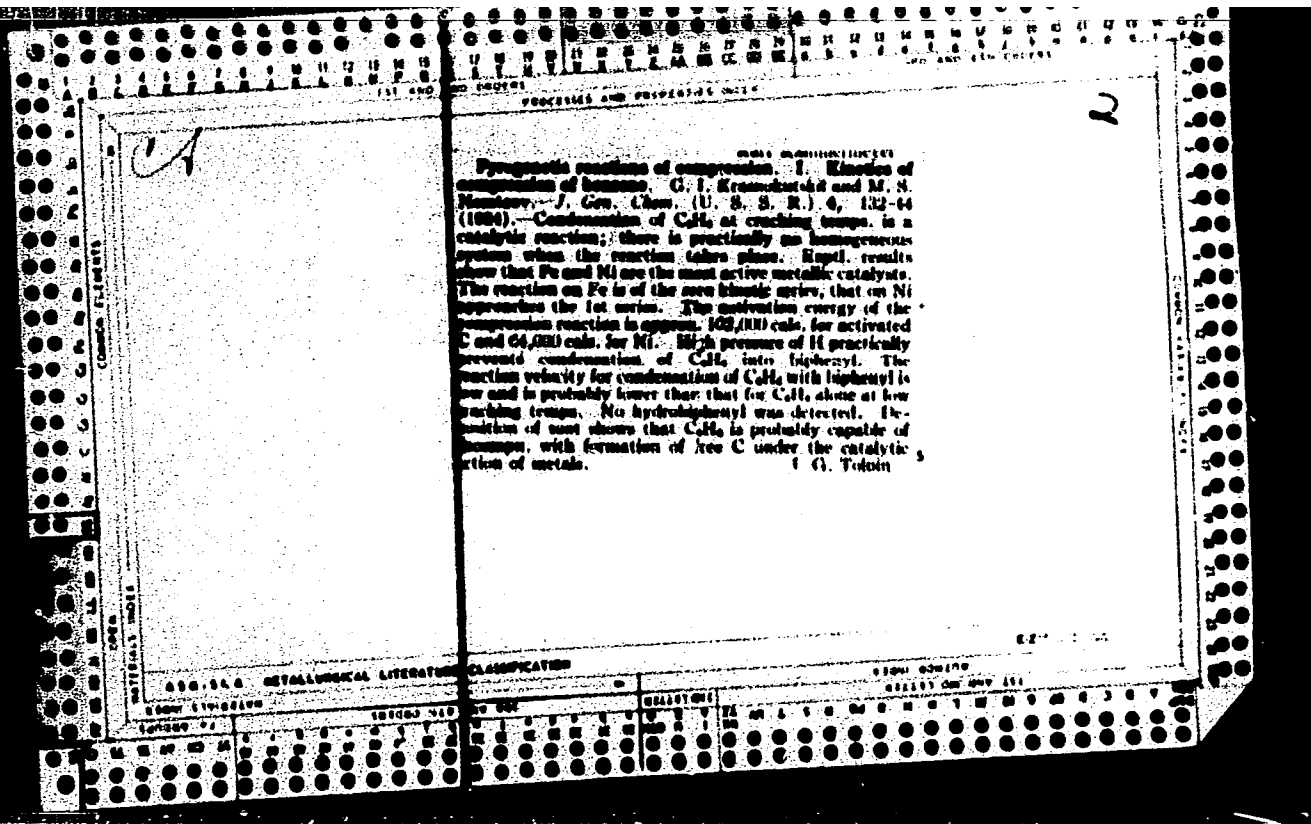
METALIMNICAL LITERATURE CLASSIFICATION

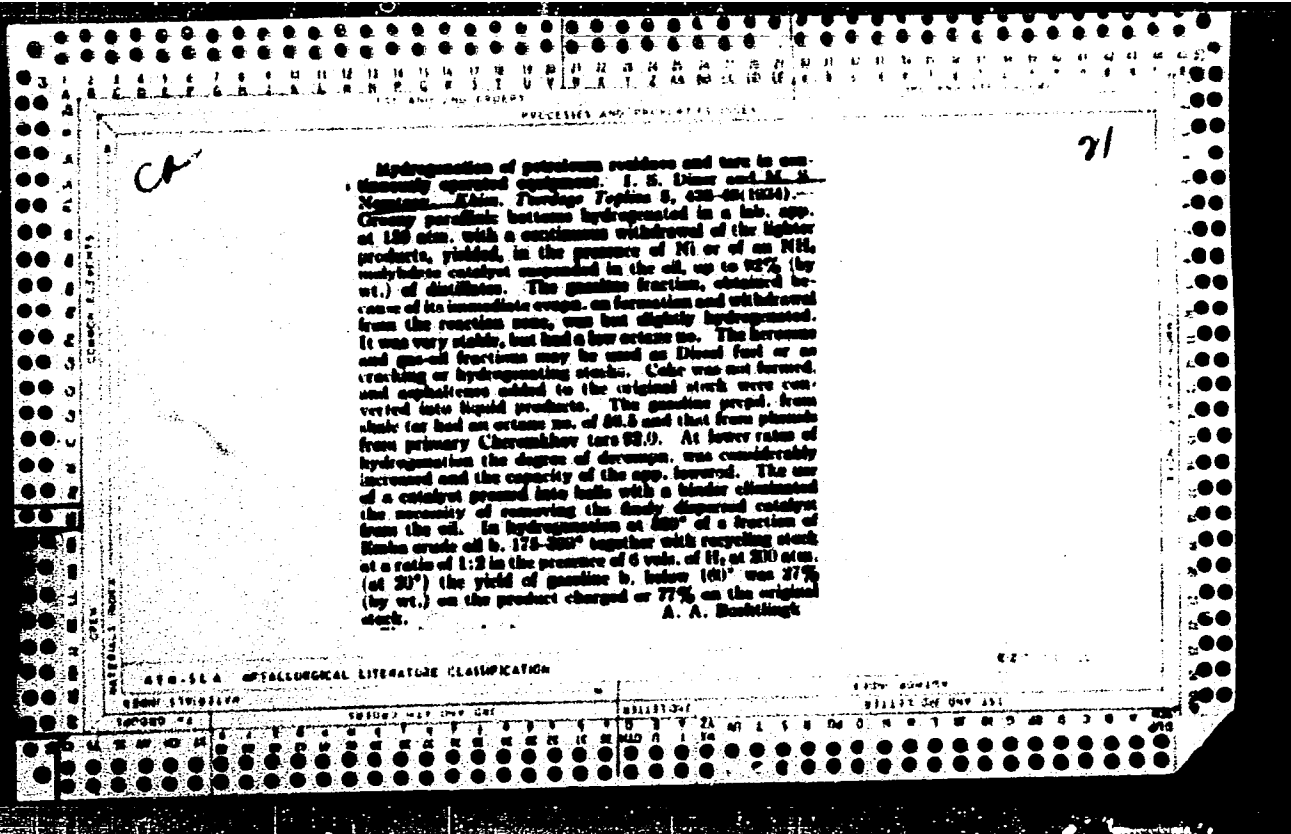
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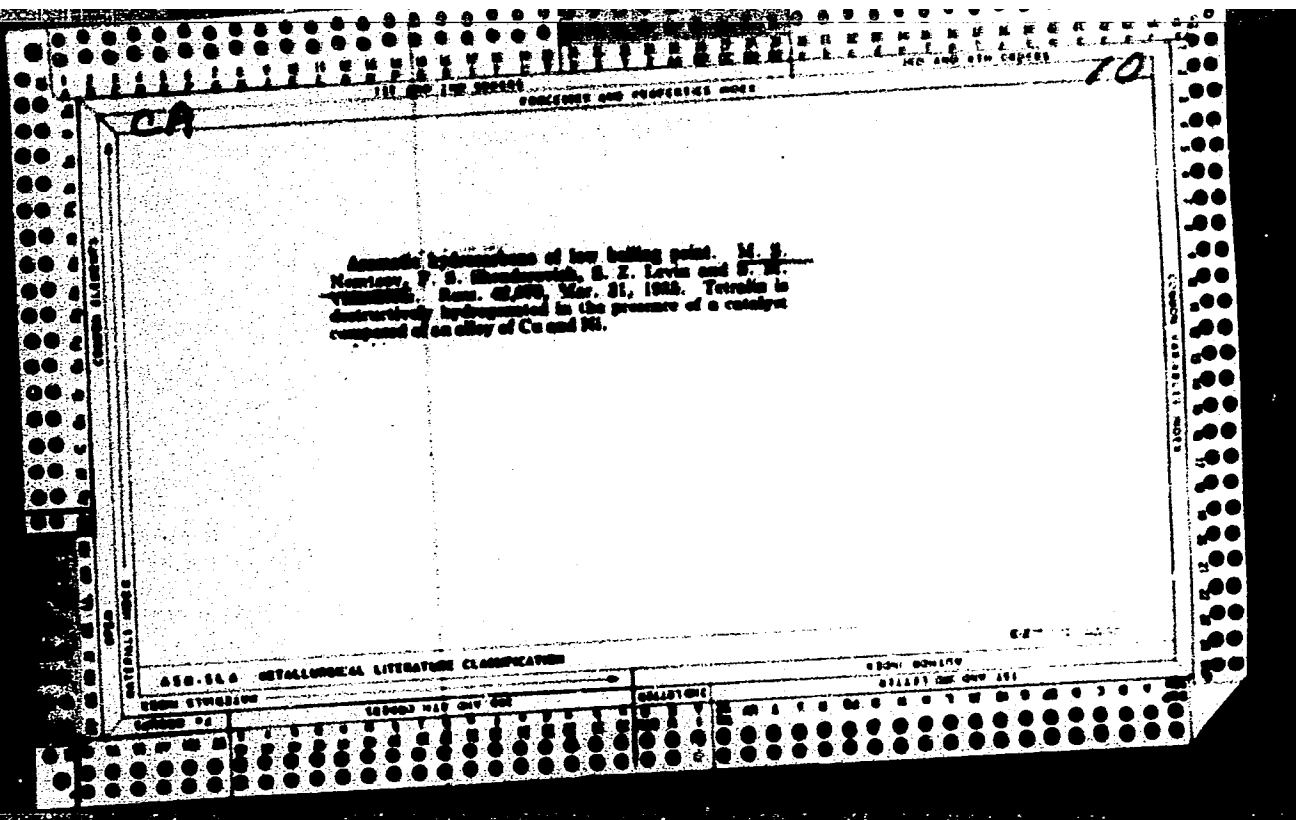
RESEARCH OR DEV. PROJ.

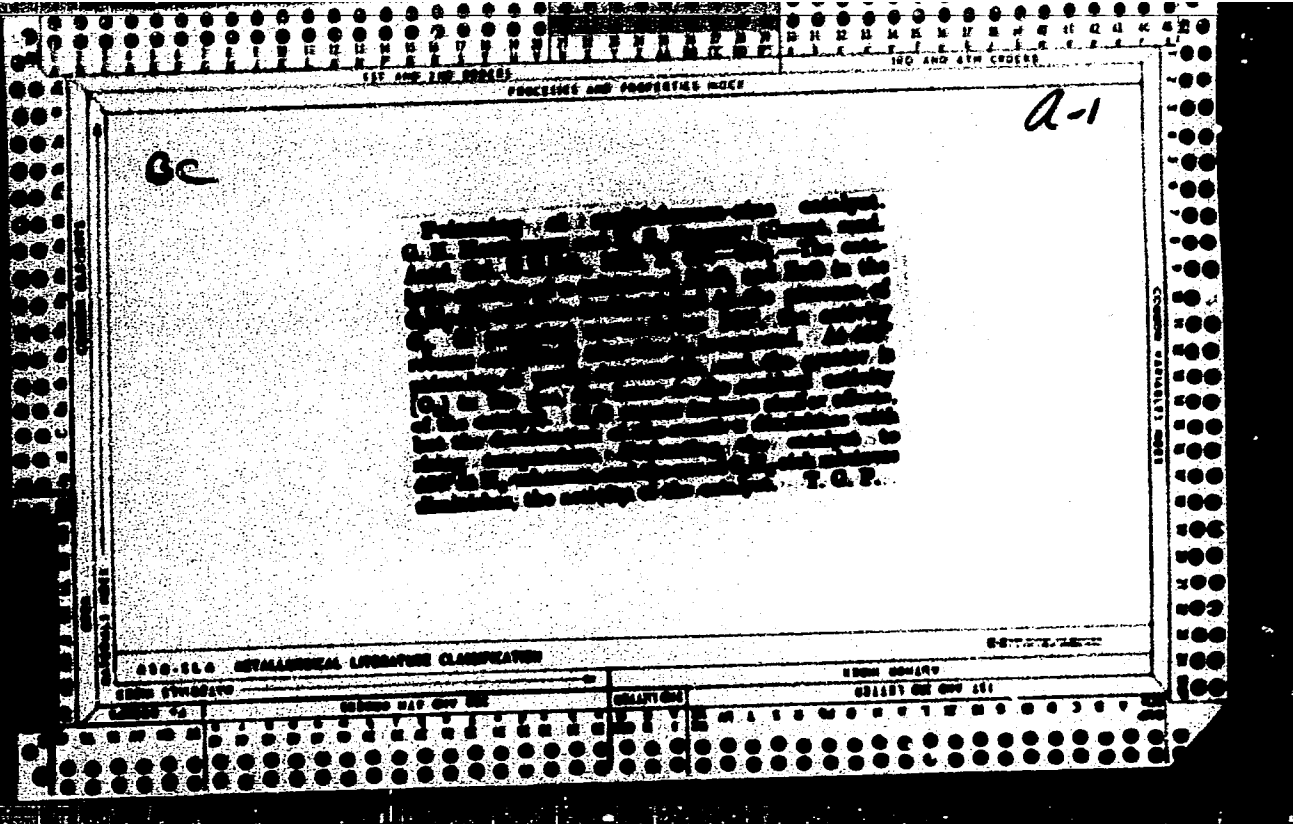
ORIGINATOR

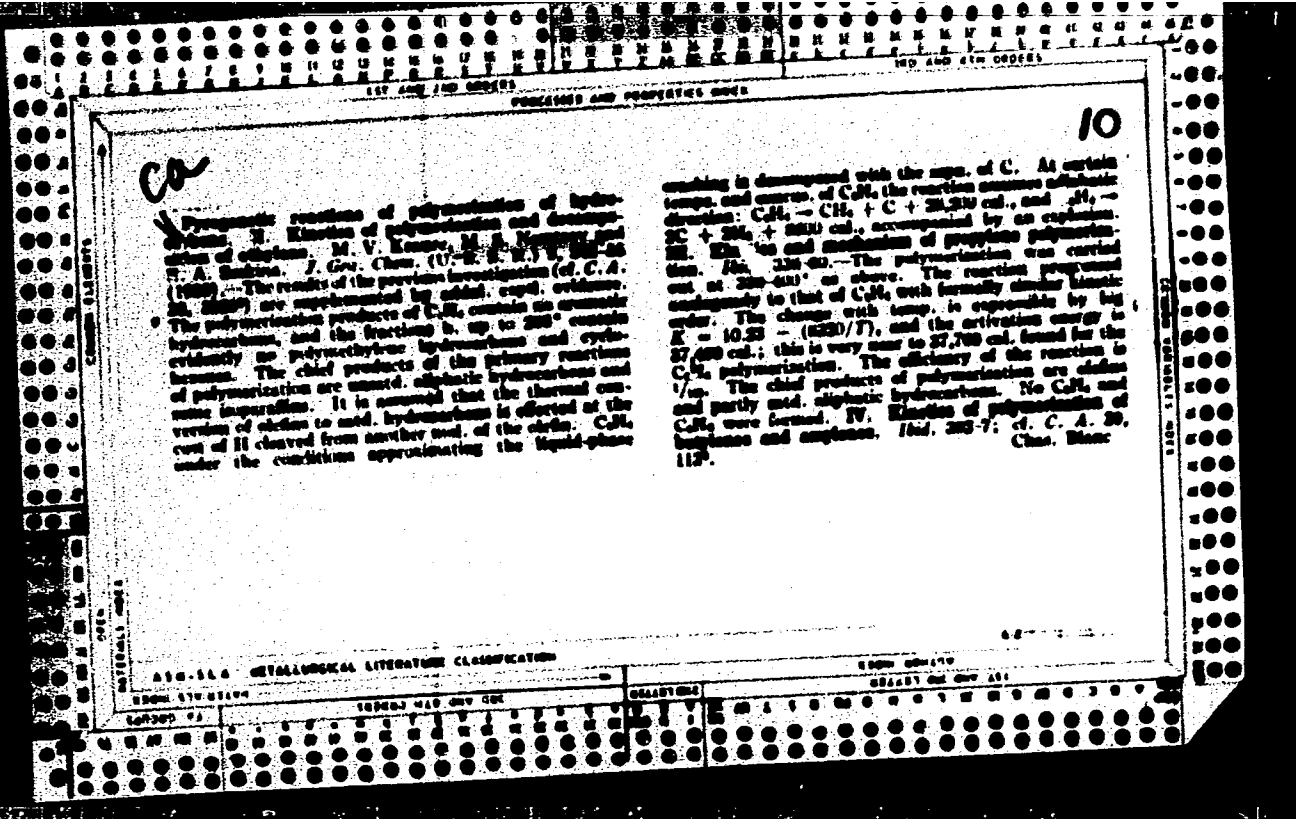
RESEARCH OR DEV. PROJ.

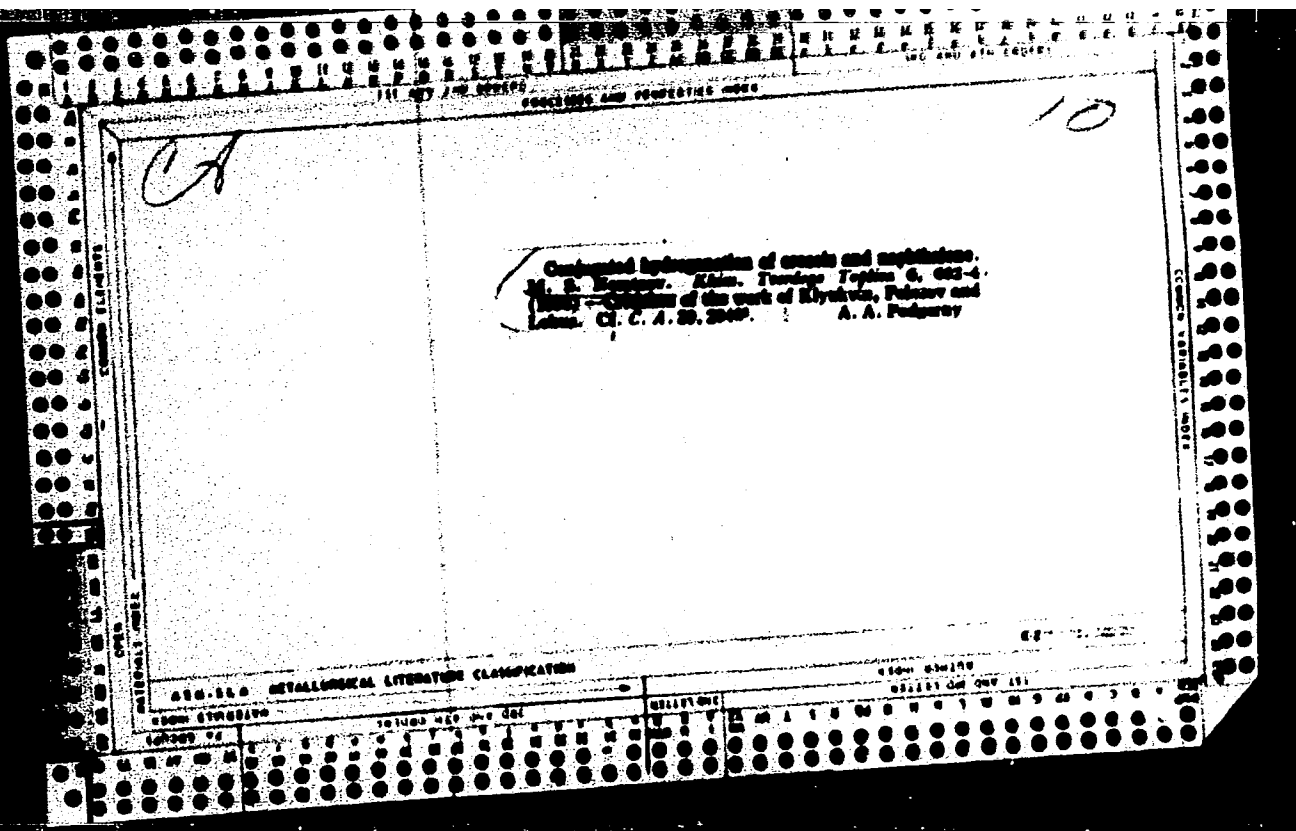


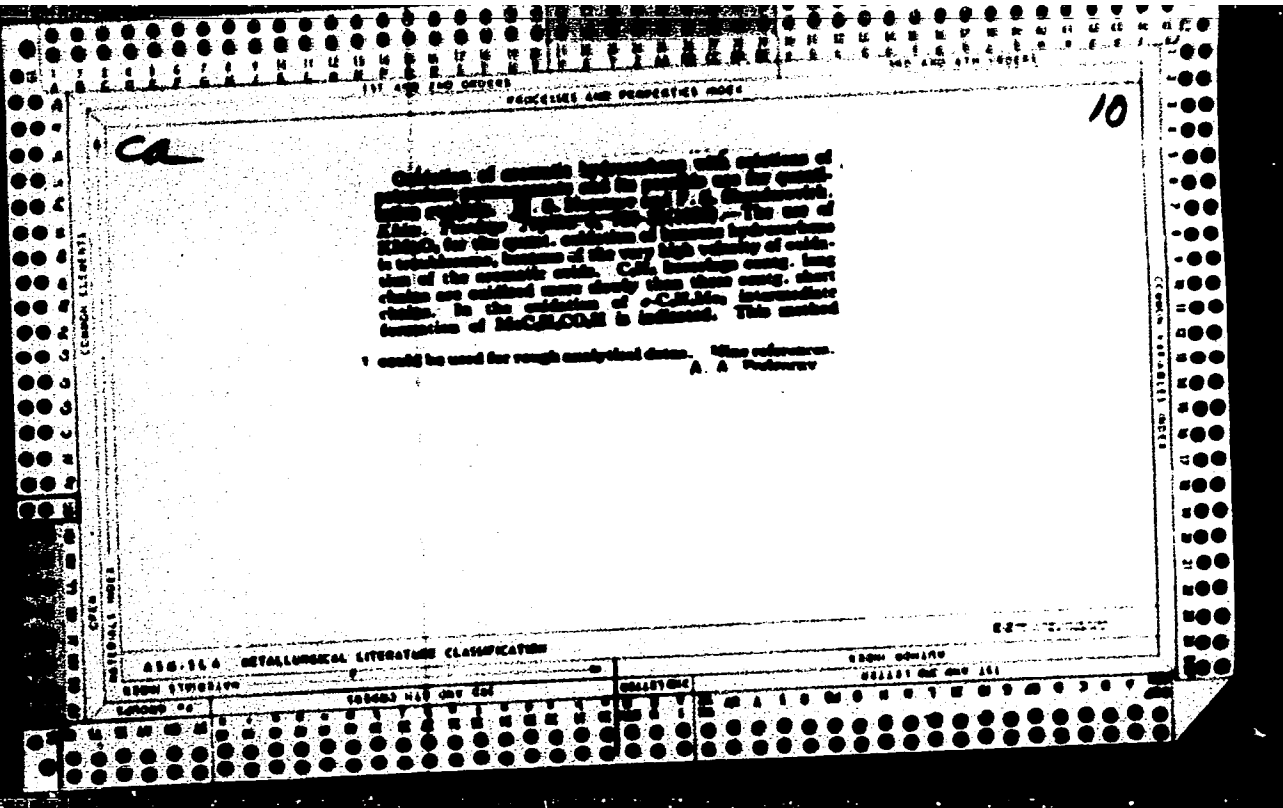


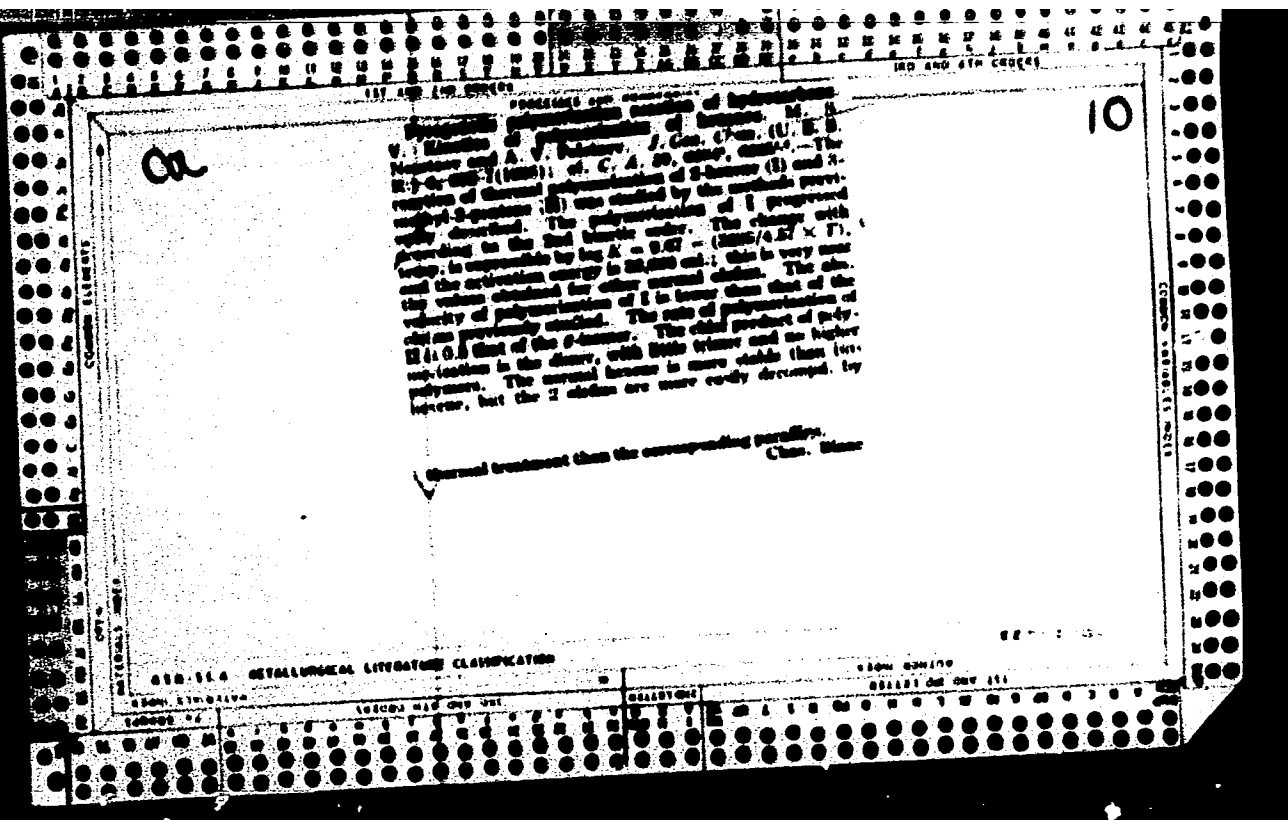


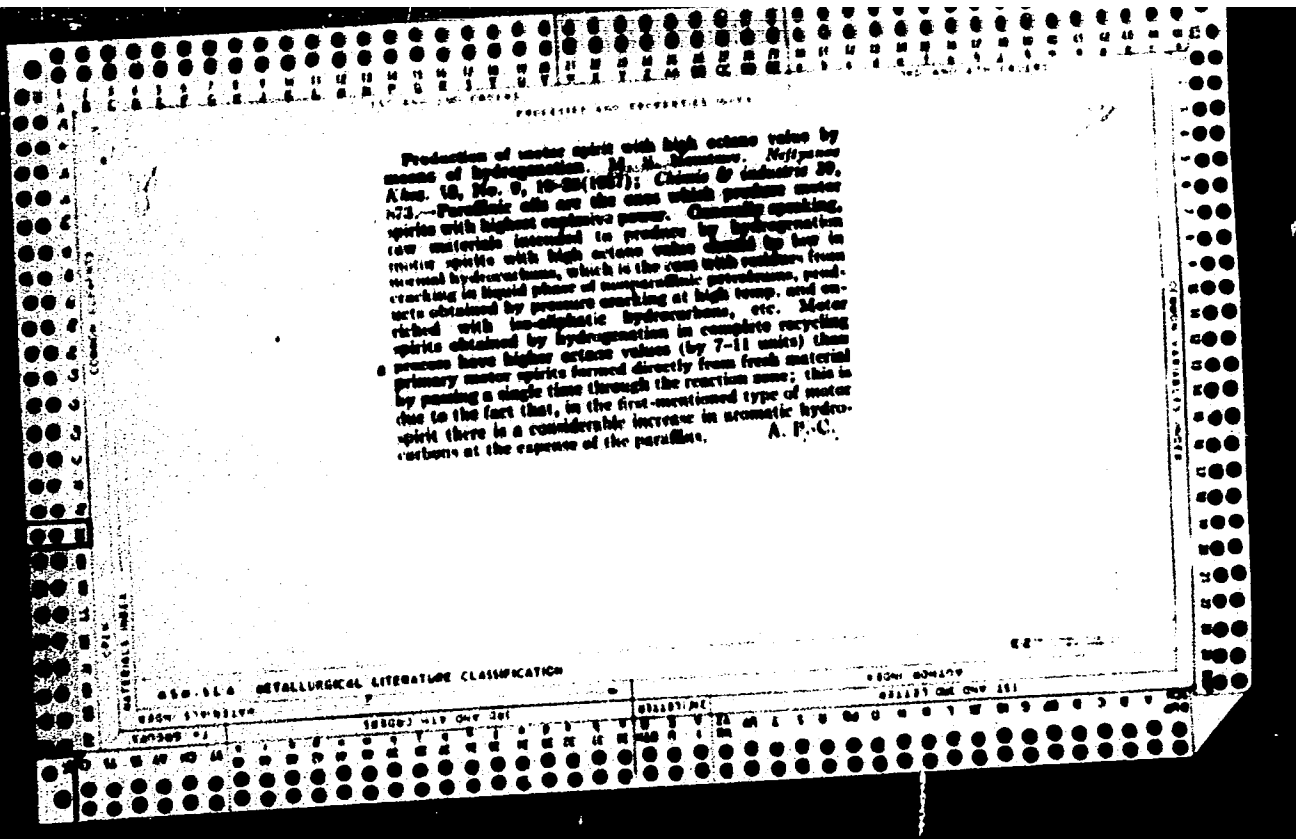


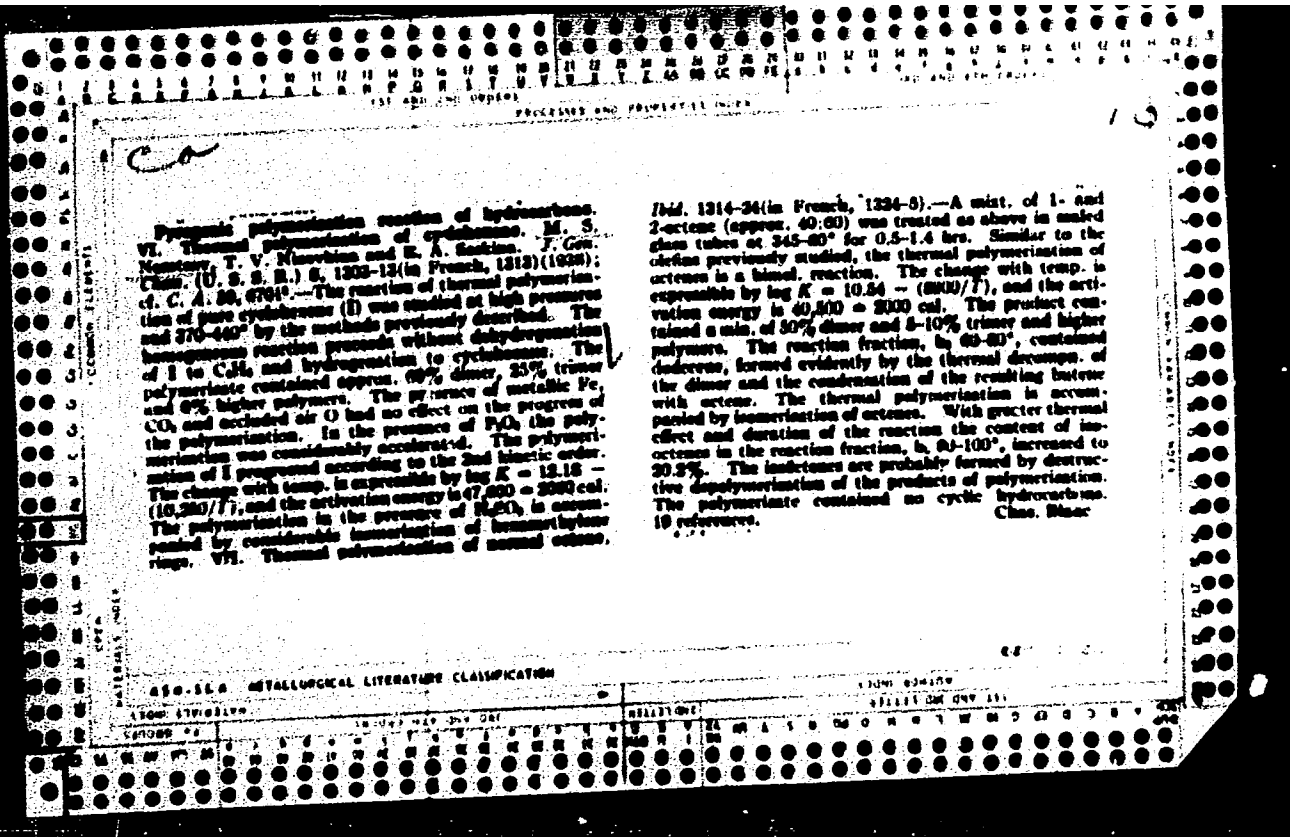


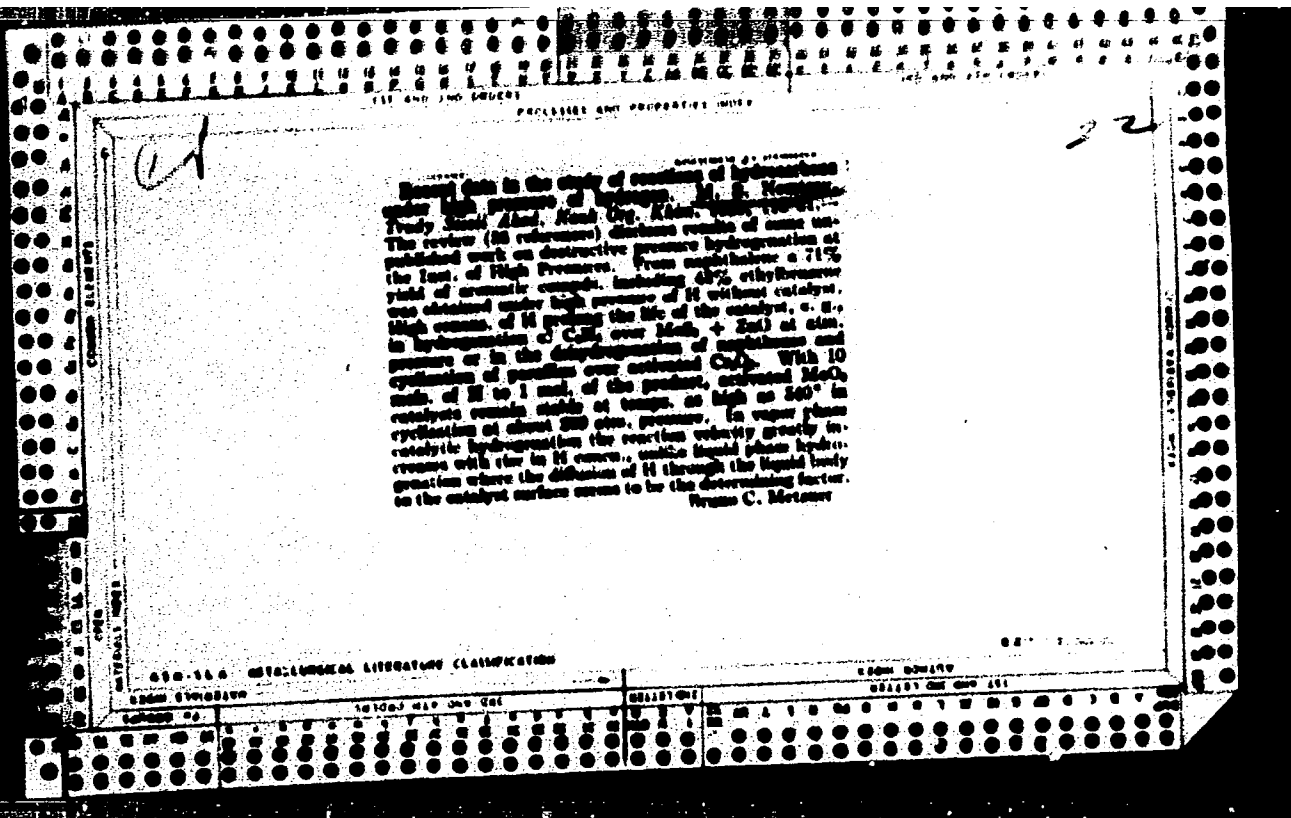












NEITSOV, N.S.

**Removing isobutylene from cracking gas. Patent U.S.S.R. 77,929. Dec.31,
1949.
(CA 47 no.19:10218 '53)**

USSR/Chemistry - Catalysis; Formaldehyde Mar 52

"Investigations in the Field of Acid Catalysis. I. Kinetics and Mechanism of the Reaction of Formaldehyde in Acidic Aqueous Solutions," N. P. Kozlov, K. M. Trankh, All-Union Sci Res Inst of Synthetic Rubber Issue 8. V. Izobedev

"Zhur Oshchek Khim" Vol XIII, No 3, pp 415-419

Actual concn of methyl formate in reaction products is larger than equill quantity, confirming Tishchenko's assumption of formation of intermediate ester. Camissaro-Tishchenko reaction proceeds in 2 stages, with rate of reaction detd by 2 parallel reactions. Kinetic eq was studied. Order of

209539

USSR/Chemistry - Catalysis; Formaldehyde Mar 52 (contd)

magnitude of equill const of formation was detd. Approx const of rate of reaction between active complexes and between complexes and free mols of methylene glycol were detd. In addn to normal formyl ion methylal is formed in the reaction between formaldehyde and the methanol which forms.

209539

HEMISOV, M. S.

WIDER USE OF MODERN THEORY.

Wider use of modern theory in the development of new technological
processes. Khim. prom. no. 6: 321-324 S '56. (NDA 10:2)
(Chemistry, Technical)

Distr: ~~SECRET~~

Simultaneous production of phenol and acetone. P. G. Sergeev, R. Yu. Ulag, B. D. Kravtsov, and G. S. Nematov. ~~USSR~~

The process is a continuous one and a catalyst continuously to a circulating, closed-cycle stream of the reaction products, and simultaneously, removing the excess of reaction products. M. Heach

NEMTSOV, M.S.

FROST, Andrey Vladimirovich, prof. [deceased]: Prinsipali uchastnye:
BUSHMAKIN, I.M.; VVEDENSKIY, A.A.; GRYAZNOV, V.M.; DEMENT'YEVA,
M.I.; DIMITSIS, A.I.; DOBROMRAVOV, B.K.; ZHARKOVA, V.R.; ZHERKO,
A.V.; IPAT'YEV, V.N.; KYATKOVSKIY, D.A.; KOROBV, V.V.; MOOR,
V.G.; NEMTSOV, M.S.; RAKOVSKIY, A.V.; RIMIZ, Ye.K.; RUDKOVSKIY,
D.M.; RYSAKOV, M.V.; SREBRYAKOVA, Ye.K.; STEPUKHOVICH, A.D.;
STRIGALOVA, N.V.; TATVSKIY, V.M.; TILICHYEV, M.D.; TRIFEL',
A.G.; FROST, O.I.; SHILYAYEVA, L.V.; SHCHUKIN, V.V.; DOLGOPOLOV,
N.N., sostavitel'; GERASIMOV, Ya.I., etv.red.; SMIRNOVA, I.V., red.;
TOPCHIYEVA, K.V.; YASTREBOV, V.V., red.; KONDRASHKOVA, S.P., red.
isd-va; LAZAREVA, L.V., tekhn.red.

[Selected scientific works] Izbrannye nauchnye trudy. Moskva,
Izd-vo Mosk.univ., 1960. 512 p. (MIRA 13:5)

1. Chlen-korrespondent AN SSSR (for Gerasimov).
(Chemistry, Physical and theoretical)

S/064/60/000/008/005/008
B020/B060

AUTHOR: Nemtsov, M. S.

TITLE: Kinetic Rules Governing the Interaction of Olefins With Sulfuric Acid

PERIODICAL: Khimicheskaya promyshlennost', 1960, No. 8, pp. 15-23

TEXT: The results obtained by H. S. Davis and collaborators (Refs. 1-3) lead to the conclusion that the absorption rate of olefin in sulfuric acid is directly proportional to the interface between the liquid and the gas, the partial pressure of olefin in the gas, and its physical solubility in the liquid. The reaction rate is, however, practically independent of the intensity of sulfuric acid intermixing, provided the surface layer is not disturbed. The conclusion is drawn that the reaction proceeds in a thin surface layer of the acid, in which there appears a steady concentration gradient of the reacting components, which determines the absorption rate of olefin. For the reaction in the gas washer the author derived the definitive kinetic equation

Card 1/3

Kinetic Rules Governing the Interaction of
Olefins With Sulfuric Acid

S/064/60/000/008/005/008
B020/B060

$$dx/dt = \left\{ kD / [th(h\sqrt{k/D})] \right\} \beta \sigma P_{pr} - k^1 \sigma P_{pr} \quad (8)$$

where D is the coefficient of the diffusion rate of propylene in H_2SO_4 , h the thickness of the reaction layer, β the coefficient of solubility of propylene in the reaction liquid, σ the area of the interface between liquid and gas and P_{pr} the partial pressure of propylene in the gas.

An equation is also derived for the number of gas bubbles suspended in 1 m³ of liquid:

$$n = V/P\omega v = 6V/P\omega \pi d^3 \quad (9)$$

where V is the amount of gas reduced to atmospheric pressure and led during one hour through a column cross section of 1 m², P is the pressure, ω is the ascending velocity of the gas bubbles, and v is the volume of one such bubble. Equation $L = L_0 [1 + 5w_0 (1 - ay/2)]$ (13) is then

derived, where L denotes the height of the H_2SO_4 layer on gas-bubbling, L_0 is the same without bubbling, w_0 is the linear velocity of compressed gas, a the propylene content in the initial gas, and y the converted part of propylene. The dependence of the reaction rate on the degree of saturation of the acid and on pressure is given in Table 1, while the dependence of

Card 2/3

Kinetic Rules Governing the Interaction of
Olefins With Sulfuric Acid

S/064/60/000/008/005/008
B020/B060

the reaction rate on pressure is given in Table 2. The effect of the feeding rate, the diameter of the gas washer, and the height of the bubbling layer upon the reaction rate is shown in Table 3. Fig. 1 shows the dependence of the reaction rate on the linear velocity of the gas. Table 4 gives the dependence of the reaction rate on the H_2SO_4 concentration and temperature (in a washer with screen holes 3 mm in diameter), and Fig. 2 shows the dependence of the reaction rate on the hole diameter in the gas washer. Table 5 shows the effect of acid concentration and temperature upon the absorption rate of propylene in the bubbling reaction vessel, Table 6 the effect of H_2SO_4 concentration on the absorption rate of propylene in the "steady film", and Table 7 the dependence of absorption rate of olefins by sulfuric acid on temperature. The highest selectivity of the process is attained when observing the conditions which secure the conservation of the "steady" reaction film. The following persons are mentioned: T. V. Prokof'yev, P. I. Markosov, G. I. Gol'dshteyn, L. F. Guzhanskaya, N. A. Nazarov, S. S. Khayn, A. M. Gel'bshteyn, M. I. Temkin, V. V. Pigulevskiy, and Kh. R. Rustamov. There are 2 figures, 7 tables, and 21 references: 10 Soviet, 9 US, 1 German, and 1 Japanese.

Card 3/3

HEMESOV, M.S.

Kinetic laws governing the reaction of olefins with sulfuric acid.
Khim.prom. no.8:633-641 D '60. (MIRA 13:12)

(Olefins) (Sulfuric acid) (Chemical reaction, Rate of)

8/079/60/030/05/05/074
B005/B002

AUTHORS: Simanov, V. A., Nentsov, M. S.

TITLE: Investigation of the Process of Alkaline Oxidation of Isopropylbenzene / On the Mechanism of Alkaline Initiation of the Reaction

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 5, pp. 1420-1428

TEXT: In the introduction of the present paper, a survey is given on data published with regard to the oxidation of isopropylbenzene with molecular oxygen (Refs. 1-8). R. Yu. Udris is mentioned in this connection. The authors of the present paper investigated the mechanism of the alkaline oxidation of industrial isopropylbenzene. Two samples of isopropylbenzene of different origin were used. Table 1 shows boiling ranges, iodine numbers, densities, and refractive indices of the two samples. The two iodine numbers differed considerably. The oxidation of isopropylbenzene was conducted by means of atmospheric oxygen. The unit which was used is shown in a graph and described. The oxidation degree of isopropylbenzene was calculated from the change of the refractive index

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Investigation of the Process of Alkaline Oxidation of Isopropylbenzene. On the Mechanism of Alkaline Initiation of the Reaction S/079/60/030/05/05/074
B005/B002

of the reaction mass by means of a given equation. For the determination of the refractive indices, an Abbé refractometer and also a Pulfrich refractometer of type ~~RF-23~~ (IRF-23) were used. Two figures show the influence of the sodium hydroxide amount on the oxidation rate of the two samples of isopropylbenzene. The investigations showed that during the alkaline oxidation of isopropylbenzene, the lye not only binds the acid by-products of the reaction, but also activates the radical decomposition of the isopropylbenzene-hydroperoxide. The character of this initiator action of the lye is identical with the formation mechanism of free radicals by thermal decomposition of azodinitrile of bis-isobutyric acid. The cation of the alkali liquor is of great influence on the initiator action (Table 2). The activating influence increases with increasing ion radius of the cation; RbOH therefore speeds up the decomposition of isopropylbenzene-hydroperoxide more strongly than NaOH. On the basis of the results obtained, a reaction scheme was set up for the mechanism of the alkaline oxidation of isopropylbenzene, which is given here. The investigations are described in detail. There are 7 figures, 2 tables, and 16 references: 10 Soviet, 5 English, and 1 German.

Card 2/3

Investigation of the Process of Alkaline Oxidation of Isopropylbenzene. On the Mechanism of Alkaline Initiation of the Reaction S/079/60/030/05/05/074 B005/B002 *vc*

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: June 18, 1959

Card 3/3

S/079/60/030/007/023/039/XX
B001/B066

AUTHORS: Simanov, V. A., Nemtsov, M. S.

TITLE: Investigation of the Alkaline Oxidation Process of Iso-
propyl Benzene II. Alkaline Protection of the Oxidation
Process

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 7, pp. 2153-2160

TEXT: To check their previous assumptions regarding the alkaline protection of the oxidation process (Refs. 2,4), the authors carried out experiments on the oxidation of isopropyl benzene in the presence of different alkaline additions (in an equimolecular ratio). Isopropyl benzene was obtained by alkylation with an aluminum chloride catalyst. The method of these experiments has been described in Ref. 1. The previous assumptions concerning the inhibition of the oxidation process of isopropyl benzene by means of the products of acid decomposition of its hydroperoxide were confirmed. Addition of alkaline salts of weak organic acids inhibits the acid decomposition of this hydroperoxide by binding the strong organic acids formed in the oxidation process. Unlike what is seen in the
Card 1/3

Investigation of the Alkaline Oxidation
Process of Isopropyl Benzene. II. Alkaline
Protection of the Oxidation Process

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B001/B066

presence of free alkali lye, the salts of organic acids do not activate the alkaline decomposition of the hydroperoxide of isopropyl benzene to form free radicals. Alkali salts of organic acids accelerate the above oxidation process, as compared with the process without alkaline addition. The quantitative acceleration effect depends on the nature of the anion of the acid, and is nearly inversely proportional to the strength of the acid. The undesirable impurities in commercial isopropyl benzene do not inhibit oxidation; the real inhibitors are their acid conversion products. The inhibitory impurities are strongest in the initial stage of the oxidation process, when an intensive accumulation of the inhibitory products takes place. The inhibitory action of undesirable impurities in commercial isopropyl benzene is identical with the inhibition of the oxidation process by the by-products resulting from the acid decomposition of the hydroperoxide of isopropyl benzene. Diagram 1 shows the oxidation kinetics of purified isopropyl benzene in the presence of equimolecular quantities of sodium lye and its salts; diagram 2 - oxidation kinetics of purified isopropyl benzene in the presence of sodium stearate; diagram 3 - oxidation kinetics of unpurified isopropyl benzene in the

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Investigation of the Alkaline Oxidation
Process of Isopropyl Benzene. II. Alkaline
Protection of the Oxidation Process

S/079/60/030/007/023/039/XX
B001/B066

presence of sodium stearate; diagram 4 - influence of the moment of adding sodium stearate upon the oxidation kinetics of unpurified isopropyl benzene. There are 4 figures, 2 tables, and 5 references: 4 Soviet and 1 German.

SUBMITTED: June 18, 1959

Card 3/3

HEMISOV, M.S.

Chemical processes in heterogeneous systems. Zhur.prikl.khim.
33 no.5:1075-1084 May '60. (MIRA 13:7)
(Systems (Chemistry))

S/080/60/033/007/015/020
A003/A001

AUTHORS: Ogorodnikov, S. K., Kogan, V. B., Nemtsov, M. S.

TITLE: The Properties of Binary Systems Formed by C₅ Hydrocarbons¹
(Communication 1)

PERIODICAL: Zhurnal prikladnoy khimii, 1960, Vol. 33, No. 7, pp. 1599-1607

TEXT: The development of an industrial method for obtaining isoprene by dehydration of isopentane necessitates the separation of mixtures of C₅ hydrocarbons. Data were obtained on the equilibrium between liquid and vapor in binary systems formed by C₅ hydrocarbons of various structure and also on their ability to form azeotropic mixtures with each other. The refractive index (n_D and n_C) was determined by a УПФ -23 (IRF-23) refractometer with an accuracy of $\pm 2 \cdot 10^{-5}$ in differential measurements. The boiling points of pure substances and their mixtures were determined in a Sventoslavskiy's ebulliometer (Ref. 4) with an accuracy of $\pm 0.05^\circ\text{C}$. It was shown that in the binary systems formed by isoprene with n-pentane, isopentane, isopropylethylene, methylethylene and trimethylethylene, and isopentane with isopropylethylene, and n-pentane with trimethylene, only in the n-pentane-isoprene system an azeotropic mixture

Card 1/2

S/080/60/033/007/015/020
A003/A001**The Properties of Binary Systems Formed by C₅ Hydrocarbons (Communication 1)**

is formed. Literature data on the formation of other azeotropic mixtures are incorrect. Based on the data on the properties of the azeotropic mixture n-pentane-isoprene and on the boiling point of the mixtures, it was shown that in systems composed of C₅ hydrocarbons small positive deviations from Raoult's law are observed. The deviations increase in the series olefin-diene, paraffin-olefin, paraffin-diene. The deviations from the additivity of the refractive index and the density of the solutions change in the same direction. The dependence of the activity coefficients of the components on the composition in systems formed by C₅ hydrocarbons is sufficiently well expressed by equations of the theory of regular solutions. The deviations from the perfect case in the systems olefin-diene and paraffin-olefin are very small. In calculations for engineering purposes these systems can be considered as perfect. There are 8 tables, 2 graphs and 10 references: 3 Soviet, 3 English, 2 American and 2 Belgian. ✓

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

SUBMITTED: December 26, 1959

Card 2/2

5.1160 2209, 1375, 1273

25652
S/080/60/033/012/006/024
D209/D305

AUTHORS: Ogorodnikov, S.K., Kogan, V.B., and Nemtsov, M.S.

TITLE: Liquid-vapor equilibrium in binary systems composed of methanol and hydrocarbons

PERIODICAL: Zhurnal prikladnoy khimii, v. 33, no. 12, 1960, 2685 - 2693

TEXT: The present work is a continuation of earlier investigations in which it was shown that mixtures of some C₅ hydrocarbons cannot be separated by straight fractionation due to the low values of their corresponding coefficients of relative volatility (α). The authors have now decided to study the possibility of increasing the relative volatility of hydrocarbons adding to the latter substances acting as separating agents in azeotropic and extractive rectification. Among possible separating agents, polar compound received greatest attention. Although the use of methanol for the above purpose has been discussed earlier, very little has been

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Liquid-vapor equilibrium in ...

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written about binary systems consisting of methanol and hydrocarbons having an equal number of carbon atoms (isologs). The liquid-vapor equilibrium was studied using a modified Gillespie apparatus, in which the thermocouple pocket was placed directly in the separator. For control purposes some of the experiments were conducted in Bushmakin apparatus devised by L.N. Bushmakin (Ref. 16: Z. P. Kh. v. 32, no. 4, 1959, p. 812) and the boiling point of the corresponding mixtures was measured in the Sventoslavskiy ebulliometer at a pressure of 760 mm Hg. The experimental data was then verified thermodynamically using the Redlich-Kister method and the relation of

$$\log \frac{\gamma_{\text{methanol}}}{\gamma_{\text{hydrocarbon}}} \quad (\gamma = \text{activity coefficient})$$

to liquid composition are represented graphically for paraffins, olefines and dienes. The curves obtained confirm that the experimental results are in agreement with a condition stipulated by the Redlich-Kister equation, i.e. the areas between the upper and low-

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Liquid-vapor equilibrium in ...

er part of the $\log \gamma_M/\gamma_H = f(x)$ and abscisse are equal (where x is the methanol content in the liquid phase). For methanol-paraffin and methanol-diene systems the difference between the two areas is almost negligible but for the methanol olefine system this difference is considerably bigger. This is probably caused by inaccuracy of measurements in high methanol concentrations. The direct relation is shown between activity coefficients of components and composition of methanol-olefine systems. From the practical point of view values obtained for one hydrocarbon may be utilized for determining the properties of systems containing its isomers and homologues. The second important point which follows from this result is that the addition of methanol to oliphatic hydrocarbon mixtures cannot practically improve the conditions of separation of isomers and homologues as compared with ordinary rectification. Maximum deviation from ideal conditions is shown by the comparatively high absolute values of $\log \gamma_M/\gamma_H$ and S-shape of the corresponding curves in the methanol-paraffin system. Straightening of the curve and reduction of $\log \gamma_M/\gamma_H$ values for olefinic and diene

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Liquid-vapor equilibrium in ...

hydrocarbons indicates that the addition of methanol to those systems should increase the relative volatility of the hydrocarbon. However, in general, it may be said that methanol is not suitable as a separating agent for the rectification of isomer mixtures of the same class. There are 6 figures, 10 tables and 21 references: 10 Soviet-bloc and 11 non-Soviet-bloc. The 4 most recent references to the English-language publications read as follows: Chu Ju Chin, R.I. Getty, L.F. Brennecke, R. Paul: Distillation equilibrium data N.I., 1950; G. Scatchard, L.B. Ticknor: J. Am. Chem. Soc. 74, 13, 3724, 1952; O. Redlich, A.T. Kister: Ind. Eng. Chem. 40, 2, 345, 1948; G. Scatchard, S.E. Wood, I.M. Mochel: J. Am. Chem. Soc., 68, 10, 1957, 1946. X

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

SUBMITTED: April 4, 1960

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20806

S/138/61/000/002/002/008
A051/A129

15.9200 2209, 1372, 1451.

AUTHORS: Nemtsov, M.S.; Shenderovich, F.S.

TITLE: The modification of colophony for producing emulsifiers to be used in the production of butadiene-styrene rubbers

PERIODICAL: Kauchuk i rezina, no. 2, 1961, 4 - 11

TEXT: According to available literature data (Table 1) the authors conclude that resin acids containing conjugated double bonds have the strongest retarding effect on the process of "hot" copolymerization of butadiene with styrene. These bonds are thought to be the main reason for the disruption in the normal polymerization process and, thus, the cause of ordinary colophony being unsuitable for technical use. The main task in modifying colophony is thought to be the removal of the compounds containing the conjugated bonds. The two main chemical transformations suggested for this purpose are hydration and disproportionation (see scheme). Both processes are based on the destruction of the conjugated double bonds, either by the addition of hydrogen or as a result of its splitting-off. The disproportionation differs from the hydration in the source of the hydrogen used and the presence of compounds with an aromatic nucleus (dehydroresin acids)

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A051/A129

The modification of colophony....

in the products of reaction. Extensive research was carried out in the Soviet Union, in order to determine which of the two processes to use for the modification process of colophony and the production of colophony emulsifiers for the SR Industry. Hydration work was carried out at the Yaroslavl' (Ref. 4) and Voronezh (Ref. 6) SR Plants and at the VNIISK. Disproportionation was systematically carried out at the VNIISK and at the VNIINEftekhim. The present article deals with the main summary of these works and the further methods for perfecting the developed processes. Several types of nickel catalysts were tested and the industrial "nickel on diatomaceous earth" used in the petroleum industry was found to be the most active one. Certain relationships between the pressure of hydrogen and the rate of its absorption in the hydration of colophony on the above-mentioned catalyst were derived which led to the following conclusions: 1) The maximum quantity of the absorbed hydrogen increases with the pressure of the latter assumed to be connected with the state of equilibrium. 2) The rate of hydration increases proportionately to the hydrogen pressure (Fig. 1). 3) The stoichiometric difference in the experiment at $p_{H_2} = 1.2$ atm between the residual content of the abietic acids (2.4%) and the quantity of the absorbed hydrogen (0.42 moles to 1 mole of acid) leads to the conclusion that at low pressures of hydrogen, simultaneously with the hydration on an active catalyst, the reactions of disproportionation may

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The modification of colophony....

take place at a sufficiently high rate; 4) The harmful reaction of the splitting-off of the carboxyl group, the specific gravity of which drops with an increase in the hydrogen pressure takes place at a sufficiently high rate simultaneously with the hydration on the nickel catalyst. The consumption of the catalyst during the hydration process was tested on two types of nickel catalyst, using two different methods of transformation depth control (Figs. 2, 3). The results seen on the graphs are explained by the fact that the initial colophony contains catalytic "poisons", which irreversibly block the active surface of the catalyst and bring about the deactivation of a certain amount of the submerged contact, the value of which depends on the concentration of the "poisons" in the colophony. Conclusions are drawn from the experimental results that the isomerization reactions of the resin acids with the nickel contact do not catalyze, i.e., they take place homogeneously (thermally). The average rates of reaction were determined in order to establish the relationship of the hydration rate to the quantity of the catalyst from the curves in the experiment with 2, 4 and 8% "Ni-Cu" of the contact (Fig. 3, dotted lines, and Fig. 4). The relationship was found to be $k = v(S - a)$, where v is the rate of reaction, k - constant of the rate of reaction, S - quantity of the submerged catalyst, % of the colophony weight, a - the quantity of the irreversibly poisoned catalyst (for the given case the value some-

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what exceeds 1% of the colophony weight). The relationships are thought to explain the insufficient stability and relatively low production indices of the experimental-industrial hydration of colophony at the Voronezhskiy zhirkombinat (Voronezh Fat Combine). The authors conclude with respect to the hydration process that in the case of colophony it could be accompanied by reactions of disproportionation if the applied catalyst has sufficient activity for this purpose. In the case of disproportionation, "Ni on diatomaceous earth" proved to be applicable as catalyst yielding a product of reaction with a sufficiently low content of abietic acids. Comparisons were made of the colophonies obtained during the process of low-temperature ampoule copolymerization of butadiene with styrene according to a trilon-rongalite formulation at the VNIISK. Obtained results showed that in the first approximation both methods give satisfactory emulsifiers to the same degree. The initial non-modified colophony is unsuitable for the polymerization process. The quantity of nickel catalyst was found to have the same effect on the disproportionation process of colophony as on the hydration process, i.e., at low quantities of the contact the rate of reaction is very low. There is a partial poisoning of the catalyst (Table 4) and substantial splitting-off of the carbonic acid. A decrease in the specific gravity of the decarboxylation can be accomplished by a thermodynamic shift to the left of the state of equilibrium:

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$\text{RCOOH} \rightleftharpoons \text{RH} + \text{CO}_2$, achieved by increasing the partial pressure of the carbonic acid. The large batches VNIISK-produced of disproportionated colophony on "Ni on diatomaceous earth" were tested and proved to be of satisfactory quality. However, the disproportionation process on the nickel catalysts was considered unpractical for industrial use, since this catalyst speeds up, in addition to the main reaction, the non-desirable splitting-off of the carbonic acid with a loss of 10% and more of resin acids. Palladium was tested in this connection to be used as a catalyst. Conclusions were drawn here that palladium is subjected to poisoning by the "poisons" present in the colophony during the process. The application of the palladium catalyst was found to decrease the raw material losses due to practical removal of the decarboxylation reactions and is cheaper as a catalyst. Experiments at the VNIISK showed that the specific activity of a unit weight of palladium exceeds that of nickel by 450 times. There are 6 figures, 6 tables and 12 references: 9 Soviet and 3 English. X

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

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The modification of colophony....

Table 1: Comparison of the "activity" of sodium soaps of colophony acids of various structure used as emulsifiers in the production of butadiene-styrene rubbers of the GRS type.

Resin acid	Yield of the polymer in 14 hours at 50°C, %		
	Hays et al. (Ref. 1)	Azorlosa (Ref. 2)	Carr et al. (Ref. 3)
Abietic	Traces	8	-
Neobietic	-	0	-
Levo-pimaric	-	0	-
Dextro-pimaric	-	75	-
Isodextropimaric	-	66	-
Tetrahydroabietic	82	83	83
Dehydroabietic	80	79	78
Dydroabietic	71	71	58
Dresinate 731	-	-	65

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The modification of colophony....

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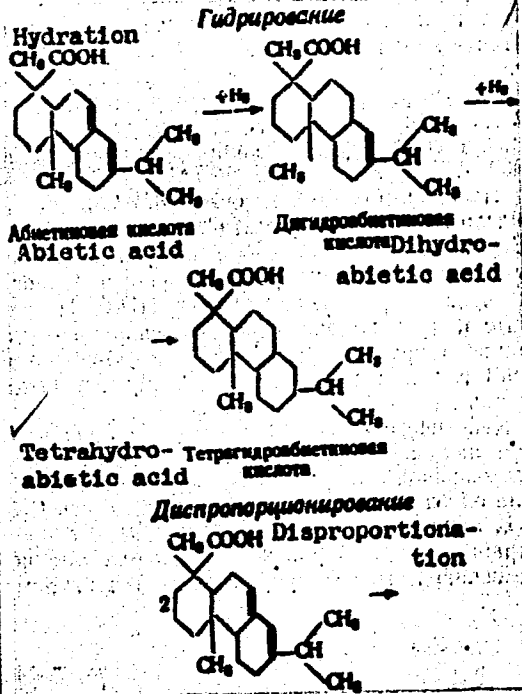
Table 4: Effect of the quantity of the catalyst "Ni on diatomaceous earth" on the rate of the disproportionation of colophony (temperature 235°; pressure of carbonic acid 5 atm; initial colophony: content of abietic acids - 67%; acid number 168 mg KOH/g)

Quantity of catalyst, % of the colophony weight	Duration of disproportionation, hours	Residual content of abietic acids, %	Acid number, mg/KOH/g
1	4	26	158
2	3	24	160
3	1	20	156

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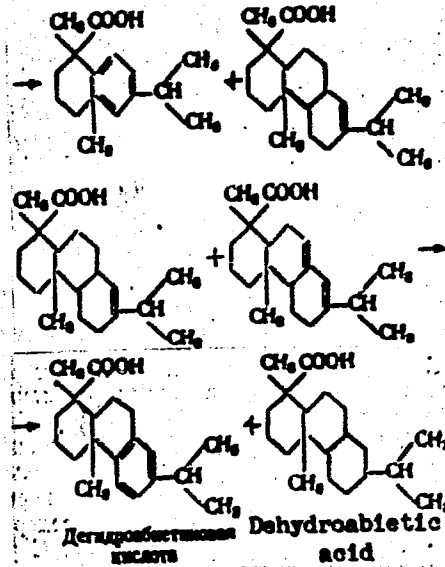
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The modification of colophony....

The scheme



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S/138/61/000/004/002/006
A051/A129

AUTHORS: Nemtsov, M.S., Ryskin, M.I.

TITLE: Disproportionation of colophony in stationary catalysts for producing emulsifiers used in the production of butadiene-styrene rubbers

PERIODICAL: Kauchuk i rezina, no. 4, 1961, 7-15

TEXT: This is a continuation of the work published in Ref. 1, M.S. Nemtsov, F.S. Shenderovich, Kauchuk i rezina, no. 2, 1961, 4. In 1959 the possibilities were studied for creating a continuous process of disproportionation of colophony with a stationary catalyst, almost excluding a catalyst suspension in the produced colophony. The major obstacle for the commercial use of this process was the gradual poisoning of the catalyst. The reactors of the model set-up (capacity 1 and 10 l) were hollow tubes. In testing the nickel catalyst the first laboratory tests showed the possibility of achieving a continuous process over a period of 500 hours at 225-230°C. The first experiments on the effect of the palladium quantity in the catalyst showed that the duration of the
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Disproportionation of colophony ...

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AD51/A129

regenerating catalyst action depends largely on the quantity of the palladium. When using a catalyst made of palladium applied on granulated large-porous activated **БAY-3** (BAU) carbon (2.3%) favorable process indexes were maintained. It was concluded that the duration of the catalyst activity increases when the initial colophony is purified of any catalytic "poisons". The effectiveness of the action of the palladium catalyst depends on the size of its grains. Recuperated activated **AP-3** (AR) carbon was used as the carrier instead of BAU-3. The relationship between the depth of transformation of abietic acid to the rate of the colophony supply and temperature was established in order to determine the kinetic laws of the disproportionation process (Fig. 6). The thermal effect of the process was also investigated. Experimental data showed that in all cases the temperature inside the catalyst was higher than in the aluminum block of the reactor, i.e. during the entire time of the catalyst action within the temperature range from 200 to 250°C the process remained exothermic. In selecting a technology and apparatus for the disproportionation process of colophony, the following factors and characteristics must be taken into account: 1) the catalyst gradually loses its activity and must be periodically replaced by a fresh one; 2)

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A051/A129

in order to maintain the necessary depth of transformation and the given output of the apparatus of continuous action of the process, the temperature conditions of the process should change with the time; 3) the positive thermal effect of the reaction calls for a regenerating heat-remover. The principle diagram of the set-up is given in Fig. 9. This scheme is thought to be typical. The quality of the disproportionated colophony as an emulsifier for the production of butadiene-styrene rubber was tested. It was found that the suspended dust-like particles of the catalyst, such as the nickel or palladium particles are present only in the first samples of colophony, rinsing the surface of the freshly-suspended catalyst grains. After 0.5-1.0 hrs of the catalyst action, the yielded product is almost completely devoid of any suspended particles. Various samples obtained during the process of "cold" copolymerization of butadiene and styrene according to the trilon-rongalite composition were tested according to the ampoule method, in order to establish the effect on the colophony emulsifiers' "activity" of the conditions of the process of colophony disproportionation. It was shown that the colophony obtained with a nickel catalyst, both directly as well as after fractionating, is much inferior in "activity" to the American preparation

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Disproportionation of colophony ...

S/138/61/000/004/002/006
A051/A129

"Dresinate - 214". The colophony disproportionated with the palladium catalyst after fractionation has about the same rate of polymerization as "Dresinate-214". Thus, the process of disproportionation with stationary palladium catalyst yields the production of effective colophony emulsifiers. There are 9 graphs, 1 diagram and 3 references: 1 Soviet-bloc and 2 non-Soviet-bloc.

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut nefte-khimicheskikh protsessov (All-Union Scientific-Research Institute of the Oil-Chemical Processes)

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5.3400

31188

S/079/61/031/012/001/011
D227/D301

AUTHORS: Belyayev, V. A., and Nemtsov, M. S.

TITLE: The decomposition of iso-propyl benzene hydrogen peroxide with alkali. I. Some properties of the aqueous sodium salt of iso-propyl benzene hydrogen peroxide

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 12, 1961, 3855-3860

TEXT: The mechanism of decomposition of iso-propyl benzene hydrogen peroxide with concentrated sodium hydroxide (first stage in α -methyl styrene production) has not so far been explained satisfactorily. It was, therefore, necessary to conduct a detailed study of the properties of the aqueous sodium salt of iso-propyl benzene hydrogen peroxide which according to the earlier works represents a primary intermediate product. The usual decomposition is conducted in heterogeneous two-phase systems and in the first place the solubility of the aqueous hydrogen peroxide salt in both the phases must be considered. It was found that at 20°C the solubility of the

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S/079/61/031/012/001/011
D227/D301

The decomposition of iso-propyl ...

salt decreased as the concentration of NaOH increased. In the two-phase system this would cause the displacement of the salt into the hydrocarbon layer. The solubility of the hydrated salt in iso-propyl benzene has been found to increase with temperature which means that under the conditions of decomposition (elevated temperature and highly concentrated sodium hydroxide) most of the salt could be found in the hydrocarbon layer. To establish the quantitative relationship between the rate of decomposition and the ratio of free and bound hydrogen peroxide the authors conducted kinetic measurements using predetermined ratios of the latter. The results showed that at 80°C the highest rate of reaction corresponded to the molar ratio of hydrogen peroxide to its salt of 2:1, while the pure sodium salt decomposed at half that rate. At 50°C the decomposition of the pure salt did not occur which indicated certain changes taking place within the reaction system. To verify this statement a mixture of free hydrogen peroxide and its hexahydrated salt in iso-propyl benzene, in which the ROOH:ROONa ratio corresponded to the highest rate of reaction, was heated to 80°C and cooled rapidly. Well defined rectangular crystals were obtained. When the same

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system was heated to 50°C and cooled rapidly prismatic crystals were formed. Chemical analysis of both products showed that in the first case a trihydrated salt was obtained while in the second no change occurred. Heating pure hexahydrated salt to 80°C gave an unchanged product, showing that the separation of three molecules of water during the reaction with hydrogen peroxide is due to the per-solvation with the formation of the hydrated form of free iso-propyl benzene hydrogen peroxide. The existence of such a salt has so far been unknown. It may, therefore, be assumed that similar results would be obtained by replacing hydrogen peroxide with other compounds capable of hydrate formation, e.g. dimethyl phenyl carbinol which is formed as a result of the decomposition of iso-propyl benzene hydrogen peroxide with alkali. Again the hexahydrated salt and dimethyl phenyl carbinol were heated to 50 and 80°C and as expected prismatic and plate-like crystals respectively were obtained. The reaction of persolvation of the hexahydrate of hydrogen peroxide when it is reacted with water acceptor A may be represented as follows:

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The decomposition of iso-propyl ...

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D227/D301

The possibility of the following reversible reactions: $\text{ROONa} \cdot 3\text{H}_2\text{O} + n\text{ROOH} \rightleftharpoons \text{ROONa} + n\text{ROOH} \cdot 3\text{H}_2\text{O}$ cannot, however, be eliminated as the displacement of the equilibrium to the left may be favored by cooling. There are 5 figures, 2 tables and 7 references: 3 Soviet-bloc and 4 non-Soviet-bloc. The references to the English-language publications read as follows: M. Kharasch, A. Fono, W. Nudenberg, J. Org. Ch., 17, 207, (1952); C. Tipper, Ind. Chem., 35, no. 3, 113 (1959); U.S. pat. 2,632,026 (1953); Ch. A. 48, 2101, (1954).

SUBMITTED: January 9, 1961

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31189

513400

S/079/61/031/012/002/011
D227/D301

AUTHORS: Belyayev, V. A., and Nemtsov, M. S.

TITLE: The decomposition of iso-propyl benzene hydrogen peroxide with alkali. II. Some properties of the anhydrous sodium salt of iso-propyl benzene hydrogen peroxide

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 12, 1961, 3861-3869

TEXT: In continuing their investigations concerning the decomposition of iso-propyl benzene hydrogen peroxide with alkali, the authors aimed at preparing an anhydrous sodium salt. The method used consisted of reacting the hydrogen peroxide salt with sodium wire, in ether, at -20 to -25°C. After the removal of solvent, dilution with n-pentane and filtration of sodium and sodium hydroxide, the product was analyzed and found to contain a mixture of dimethyl phenyl carbinol and its sodium alcoholate. Further experiments were concerned with determining a relation between the rate of the de-

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The decomposition of iso-propyl ...

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D227/D301

composition of the iso-propyl phenyl benzene hydrogen peroxide and free hydrogen peroxide. The compositions of the starting mixtures were chosen so that the content of the dimethyl phenyl carbinol and its alcoholate in relation to the total quantity of free and bound hydrogen peroxide were constant. The kinetic curves for these systems showed that the addition to the anhydrous sodium hydrogen peroxide salt of free hydrogen peroxide ($\text{ROOH} : \text{ROONa} = 1.23$) not only increased the rate of reaction, but also increased the limit of conversion. Assuming that the anhydrous salt is also stable, the addition of free hydrogen peroxide would give rise to some reactive intermediate compound which would determine the rate of reaction. The existence of the limit of conversion results then from the exhaustion of hydrogen peroxide and the thermal stability of residual sodium salt. This explanation appears to contradict the previous work, in which although the free hydrogen peroxide has not been added, a reaction was observed. In that case, however, free hydrogen peroxide might have been formed as a result of an exchange reaction between the hydrogen peroxide salt and the carbinol, X

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The quantity of hydrogen peroxide formed is determined by the end concentration of free dimethyl-phenyl carbinol. Assuming that reaction (1) takes place, introduction of dimethyl phenyl carbinol into the reaction should displace the reaction to the left and lower the limit of conversion. The results confirmed that this is the case. In preparing the anhydrous sodium salt, separation of a white solid was observed. The analysis showed that the solid represented a compound of hydrogen peroxide and its salt or dimethyl phenyl carbinol alcoholate. An attempt was then made to obtain the solid directly by mixing equimolar quantities of hydrogen peroxide and its anhydrous sodium salt at about 0°C. The product proved hygroscopic but it was possible to obtain needle-like crystals, in dry nitrogen. Chemical analysis of the latter showed that they represented a compound in which the molar ratio of active oxygen (peroxide) and the sodium ion was 2:1. This complex may be represented by the formula $(\text{ROONa} \cdot \text{ROOH})_n$. To establish the degree of

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The decomposition of iso-propyl ...

association of the complex, its molecular weight was determined by the cryoscopic method, using dry benzene. The molecular weight coincided with the molecular weight of the dimer $(ROONa \cdot ROOH)_2$; on dilution, however, a reversion to the monomer was observed. The molecular weights of iso-propyl benzene hydrogen peroxide solutions were also determined, finding that in very dilute solutions no association of the compound occurs. When the concentration was increased association occurred, but the molecular weight never reached a maximum and showed a linear increase within the experimental concentration range, indicating the formation of polymeric forms. Formation of the complex is ascribed to hydrogen bonding between the hydroxyl group of the peroxide and one of the oxygens of its sodium salt. Infrared spectra showed that the strength of the hydrogen bond was considerably higher than for the free hydrogen peroxide. The absorption line for the free OH group was absent for 1 M solution of the latter, while in the case of the complex this line appeared for 0.1 M concentrations. There are 9 figures, 3 tables and 11 references: 6 Soviet-bloc and 5 non-Soviet-bloc. The refe-

X

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31189

S/079/61/031/012/002/011
D227/D301

The decomposition of iso-propyl ...

rences to the English-language publications read as follows: M. Kharasch, A. Fono, W. Nudenberg, J. Org. Ch., 17, 207 (1952); M. Kharasch, A. Fono, W. Nudenberg, J. Org. Ch., 16, 113 (1951); L. Bateman, H. Hughes, J. Chem. Soc., (1952), 4594.

SUBMITTED: January 9, 1961

Card 5/5

OGORODNIKOV, S.K.; KEGAN, V.B.; NEMTSOV, M.S.

Liquid-vapor equilibrium in binary systems formed by hydrocarbons
and acetone. Zhur. prikl. khim. 34 no.2:323-331 F '61.

(MIRA 14:2)

(Acetones) (Hydrocarbons)
(Phase rule and equilibrium)

OGORODNIZKOV, S.K.; KOGAN, V .B.; NEMTSOV, N.S.

Liquid - vapor equilibrium in systems formed by hydrocarbons and
methyl formate. Zhur.prikl.khim. 34 no.3:581-584 № 161.
(MIRA 14:5)

(Formic acid) (Phase rule and equilibrium)

OGORODNIKOV, S.K.; KOGAN, V.B.; NEMTSOV, M.S.; BUROVA, G.V.;
Prinimala uchastiye: MOROZUVA, A.I.

Liquid-vapor equilibrium in binary and ternary systems of C₅
hydrocarbons and acetonitrile. Zhur. prikl. khim. 34 no.5:
1096-1102 My '61. (MIRA 16:8)

(Hydrocarbons) (Acetonitrile)
(Phase rule and equilibrium)

OGORODNIKOV, S.K.; KOGAN, VLB.; NEMTSOV, M.S.; Primali uchastiye
MOROZOVA, A.I.

Liquid - vapor equilibrium in binary and ternary systems formed
by hydrocarbons C₅ and dimethylformamide. Zhur.prikl.khim. 34
no.11:2441-2446 N⁵61. (MIRA 15:1)
(Hydrocarbons) (Formamide)
(Phase rule and equilibrium)

OGORODNIKOV, S.K.; KOGAN, V.B.; NEMTSOV, M.S.; MOROZOVA, A.I.

Correlation between polar substances and the deviations from the additivity of the index of refraction and density of hydrocarbon mixtures and the deviations from ideal behavior in the systems.

Zhur. prikl. khim. 34 no. 12:2782-2796 D '61. (MIRA 15:1)
(Hydrocarbons) (Systems (Chemistry))

S/204/62/002/006/004/012
E075/E192

AUTHORS: Genkin, A.N., Ogorodnikov, S.K., and Nemtsov, M.S.

TITLE: Application of gas-liquid chromatography for the investigation of the interaction of hydrocarbons with polar substances

PERIODICAL: Neftekhimiya, v.2, no.6, 1962, 837-844

TEXT: The authors used gas-chromatographic methods to establish a connection between the nature of C₅ hydrocarbons (solutes) and the polar solvents as well as the intensity of their interaction. The interaction was considered to be related to the relative activity coefficients of the hydrocarbons dissolved in the solvents. The relative activity coefficients γ_{rel}^n were determined from:

$$\gamma_{rel}^o = \frac{v_R^{hc.C_5}}{v_R^{n.C_5H_{12}}} \times \frac{P_{hc.C_5}^o}{P_{n.C_5H_{12}}^o}$$

where: $P_{hc.C_5}^o$ and $P_{n.C_5H_{12}}^o$ are vapour pressures of a given C₅;

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Application of gas-liquid ...

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E075/E192

hydrocarbon and n-pentane respectively; $v_R^{hc.C_5}$ and $v_R^{n.C_5H_{12}}$ are their retention volumes. The solvents investigated were: nitromethane, tetranitromethane, dimethylformamide, acetonitrile, aniline, nitrobenzole, benzonitrile and a high boiling perfluorohydrocarbon oil containing 0.2% H. The absolute activity coefficients for the paraffins, olefins and dienes in all the polar solvents tried are in the approximate ratio of 4:2:1 respectively. The polar solvents decrease the activity coefficients of the unsaturated hydrocarbon solutes from 6.14 to 0.89 in the following order: nitromethane > dimethylformamide > acetonitrile > aniline > nitrobenzole > benzonitrile > high boiling point perfluorohydrocarbon oil. This order does not follow the dipole moments of the solvents. There is, however, a strong direct correlation between the activity coefficients and the values of positive charges localized in the atom groups from which the electrons are donated to the acceptor groups. Thus the interaction with the polar solvents is a result of specific interaction of mobile π -electrons of the double bonds with the positively charged atoms of the polar solvents. Other factors influencing the interaction are due to

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steric factors (tetranitromethane gives lower activity coefficients than nitromethane, although the positive charge of the latter is smaller than that of tetranitromethane) and association of solvent molecules. The interaction of the solvent molecules with the solutes decreases if the solvent molecules associate. For the perfluorohydrocarbon oil the activity coefficients of hydrocarbons do not depend greatly on their nature, the activities decreasing with the degree of unsaturation. It is expected that this type of solute-solvent interaction will enable determination of the efficiency of separation and order of yield in gas-chromatographic methods.

There are 4 tables.

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SUBMITTED: May 30, 1962

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S/079/62/032/009/004/011
IO48/I242

AUTHORS: Simanov, V.A. and Nemtsov, M.S.

TITLE: Investigation of the alkaline oxidation of isopropylbenzene. III. Some kinetic features of the oxidation in alkaline media

PERIODICAL: Zhurnal obshchey khimii, v.32, no.9, 1962, 2914-2918

TEXT: This is the third part of a paper whose first and second parts appeared in Zhurnal obshchey khimii, v.30, 1960, pp. 1420 and 2153 respectively. It deals with the effect of Na stearate on the rate of decomposition of isopropylbenzene peroxide, of isopropylbenzene peroxide on the rate of oxidation of isopropylbenzene in the presence of Na stearate, and of NaOH on the rate of oxidation of isopropylbenzene. The thermal decomposition of isopropylbenzene peroxide in the absence of Na stearate is a self-accelerating process with a half-time of ca. 8 hrs; the addition of 1 wt % Na stearate inhibits the decomposition reaction and the amount of peroxide decomposed after 8 hours is ca. 8% of the initial amount. This effect is attributed

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I048/1242

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to the interaction of the Na stearate with some acid decomposition products which otherwise accelerate the reaction. The rate of oxidation of isopropylbenzene in a mixture with 0.3% (by wt) of Na stearate and various amounts of isopropylbenzene peroxide increased with increasing peroxide concentration in the mixture, up to a certain limiting value; the increase in the rate of oxidation was not directly proportional to the increase in peroxide concentration, this being attributed to the interference of side reactions. In another series of experiments, part of the isopropylbenzene was treated with solid NaOH before oxidation; the isopropylbenzene thus treated oxidized at a rate much higher than that of untreated isopropylbenzene; this explains the higher rate of oxidation of isopropylbenzene under industrial conditions. There are 4 figures.

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SUBMITTED: August 7, 1961
Card 2/2

S/079/62/032/009/005/011
1048/1242

AUTHORS: Simanov, V.A. and Nemtsov, M.S.

TITLE: Investigation of the alkaline oxidation of isopropylbenzene. IV. Effect of the by-products of the oxidation of isopropylbenzene

PERIODICAL: Zhurnal obshchey khimii, v.32, no.9, 1962, 2919-2925

TEXT: This is the fourth part of a paper whose first, second, and third parts appeared in Zhurnal obshchey khimii (v. 30, 1960, pp. 1420 and 2153; v. 32, 1962, p. 2914); this part deals with the effect of the most important by-products of the oxidation of isopropylbenzene on the rate of the process at 110°C. The rate of oxidation of isopropylbenzene in the presence of 0.001 - 0.1 wt % phenol was much lower than in the absence of this reagent, and the inhibiting effect of phenol was proportional to its concentration. The effect of phenol is attributed to its interaction with free radicals and the resulting decrease in free-radicals concentration in the reaction mixture. The addition of 4 moles of NaOH per mole phenol,

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practically neutralized the inhibiting effect of the phenol and the oxidation proceeded as in the absence of this reagent. Benzoquinone inhibited the oxidation of isopropylbenzene less than phenol but its effect increased in the presence of NaOH. This is attributed to the formation of compounds similar to humic acid. The addition of 1-5 wt % acetophenone had no effect on the rate of oxidation, but in the presence of NaOH the acetophenone reduced the rate of oxidation in the initial stages of the process. This is attributed to the oxidation of the acetophenone to benzoic acid, which neutralizes part of the NaOH and thus reduces the free-radical concentration in the reaction mixture. There are 7 figures and 2 tables.

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SUBMITTED: August 7, 1961

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S/079/62/032/009/006/011
I048/I242

AUTHORS: Simanov, V.A. and Nemtsov, M.S.

TITLE: Investigation of the alkaline oxidation of isopropylbenzene. V. The effect of sulfur-containing impurities

PERIODICAL: Zhurnal obshchey khimii, v.32, no.9, 1962, 2925-2929

TEXT: This is the fifth part of a paper whose previous parts appeared in Zhurnal obshchey khimii (v. 30, 1960, pp. 1420 and 2153; v. 32, 1962, pp. 2914 and 2925). This part deals with the effect of sulfur-containing impurities on the rate of oxidation of the isopropylbenzene. Precipitation of the S-containing impurities with a mercurous salt (Denigè reagent) yielded a complex solid salt which decomposed explosively on heating; decomposition of this complex (by treating with HCl) yielded an organic phase which was analysed and found to be 2-isopropylthiophene. Treatment with the mercurous salt solution reduced both the concentration of S-containing compounds (from 0.03 to 0 wt % S) and the iodine number (from 1.19 to 0.69-0.70); this shows that the mercurous salt - 2-isopropylthiophene precipitate

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contains some unsaturated compounds too. The rate of oxidation of the isopropylbenzene purified from S-containing compounds was much higher than that of the non-treated material; the isopropylbenzene peroxide content of the purified material after 6 hrs of oxidation was 17%, while that of the untreated isopropylbenzene was only 4%; moreover, the peroxide content of the purified isopropylbenzene increased on further oxidation, while that of the untreated material dropped to about 1% after 10 hrs of oxidation. The inhibiting effect of the isopropylthiophene is attributed to the strong acids it yields on oxidation; in fact, this inhibiting effect was completely eliminated if 0.3 wt % of Na stearate was added to the isopropylthiophene-containing isopropylbenzene. The rate of oxidation of isopropylbenzene purified of S-containing impurities by treatment with concentrated H_2SO_4 was slightly higher than that of isopropylbenzene purified by treatment with the mercurous salt; this is attributed to removal of larger amounts of unsaturated compounds in the sulfuric acid treatment. There is 1 figure and 2 tables.

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SUBMITTED: August 7, 1961

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S/079/62/032/010/001/008
D204/D307

AUTHORS: Belyayev, V.A., and Nemtsov, M.S.

TITLE: A study of the alkaline fission of iso-propyl benzene hydrogen peroxide. III. Kinetics of the thermal decomposition of the complex ROONa.ROOHPERIODICAL: Zhurnal obshchey khimii, v. 32, no. 10, 1962;
3113 - 3122

TEXT: The thermal decomposition of ROONa.ROOH (A), where $R = C_6H_5(CH_3)_2^-$, was studied in continuation of earlier work (ZhOKh, 31, 3861, 1961). The decomposition of A dissolved in iso-propylbenzene at 50°C was of the kinetic order ~ 1.35 w.r.t. A. This is attributed to the formation of a dimer, $[A]_2$, which decomposes more readily, the respective velocity constants for A and $[A]_2$ being in the ratio of 1 : 7. The final degree of decomposition (63 %) exceeded that demanded by $ROONa.ROOH \rightarrow ROONa + ROH + \frac{1}{2} O_2$ (50 %), owing to

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side reactions $ROONa + ROH \rightleftharpoons ROOH + RONa$ and $ROONa + PhCOOH \rightarrow ROOH + PhCOONa$. The rates and the extent of decomposition at 50°C. were considerably accelerated in the presence of polar compounds (dimethylphenyl carbinol, acetophenone, phenyl- α -naphthylamine) the effect increasing with increasing dipole moment of the additive, suggesting the formation of highly reactive complexes by dipole association. The increased tendency of higher complexes, $[A]_n$ towards decomposition is ascribed to the occurrence of reverse reactions between $ROONa$ and reaction products. The decomposition rates of $[A]_n$ are initially slowed down by free $ROOH$, owing to the formation of stabler complexes. The mechanism of the alkaline fission of $ROOH$ was shown to be the same in both anhydrous and aqueous media, although in the latter case the reaction was not accelerated in the presence of dimethylphenyl carbinol. The activation energy for the thermal decomposition of $[A]_n$ has been found to be 18 ± 0.5 kcal/mole between 30 and 50°C. There are 9 figures and 3 tables. ✓

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Scientific Research Institute of Synthetic Rubber ime-
ni S.V. Lebedev)

SUBMITTED: November 4, 1961

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S/079/62/032/010/002/008
D214/D307

AUTHORS: Simanov, V.A., and Nemtsov, M.S.

TITLE: The study of the alkaline oxidation of iso-propylbenzene. VI. The influence of organic acidsPERIODICAL: Zhurnal obshchey khimii, v. 32, no. 10, 1962,
3179 - 3183

TEXT: The aim of this work was to study the influence of organic acids on the rate and path of the oxidation reaction of iso-propylbenzene by H_2O_2 . Small quantities of $HCOOH$ did not affect the rate of this process; higher concentration (1.05 % $HCOOH$) noticeably retarded the reaction. This is thought to be due to the destruction of H_2O_2 by $HCOOH$ with the formation of CO_2 . Acetic acid did not influence the oxidation process but gallic and salicylic acids retarded the oxidation while stearic and benzoic acids accelerated the reaction. The retardation effect of the hydroxy-acids is attributed to their inhibiting action and to their ability to catalyze the decomposition of H_2O_2 . The acceleration of the reaction, by stearic

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and benzoic acids is due to the formation of unstable complexes between H_2O_2 and the acid which dissociate to give free radicals..

HCOONa also accelerates the oxidation by destroying any strong acids formed during the reaction. There are 6 figures. ✓

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SUBMITTED: August 7, 1961

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S/079/62/032/011/001/012
D204/D307

AUTHORS: Belyayev, V.A., and Nemtsov, M.S.

TITLE: A study of the alkaline fission of iso-propylbenzene hydrogen peroxide (A). IV Mechanism of the reaction

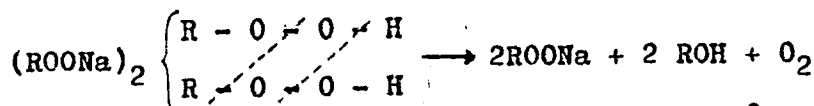
PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 11, 1962, 3483-3493

TEXT: The present paper is a continuation of earlier work (ZhOKh, 32, 3113, 1962), in which it was shown that the alkaline fission of A proceeds via the formation of $[ROONa \cdot ROOH]_n$, where $R = PhCMe_2$ and $n = 1$ or 2 (compound $[B]_n$). Consideration of published data and of the initiation of the polymerization of styrene by thermally decomposed A and B showed that free radicals may form during both thermal and alkaline fissions of A and B. The alkaline fission in anhydrous media of A is believed to proceed by (1) formation of B, largely by dipole-dipole or H-bond interactions, followed by some dimerization, (2) fission of the dimer: ↓

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(3) interaction of O_2 with the simultaneously formed R^\bullet (from the fission products RO^\bullet and OH of monomeric B, which had interacted with the solvent RH), i.e. $R^\bullet + O_2 \rightarrow ROO^\bullet$ and $ROO^\bullet + RH \rightarrow ROOH + R^\bullet$. This mechanism was confirmed by measurement of the yields of carbinol ROH during the fission reactions, in the presence and absence of p-benzoquinone. The thermal decomposition is believed to proceed mainly by O-O fission and formation of RO^\bullet , whilst the alkaline fission is chiefly the result of non-radical reaction (2). An exactly analogous mechanism is proposed for the alkaline fission of A in aqueous media. In accordance with theoretical expectations, experiments with the hydroxides of Na, K and Ba showed that the rates of fission increased with increasing field strength of the cation, (i.e. $Ba > Na > K$), and were strongly decreased in the presence of large amounts of water (owing to the aqueous decomposition of the most active $[B]_2$ complex. There are 4 figures and 4 tables.
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ni S.V. Lebedev)

SUBMITTED: November 4, 1961

Card 3/3

GENKIN, A.N.; OGORODNIKOV, S.K.; KOGAN, V.B.; NEMTSOV, M.S.; PRESMAN, B.I.

Influence of polar substances on the relative volatility of
C₅ hydrocarbons. Zhur.prikl.khim. 36 no.1:142-147 Ja '63.
(MIRA 16:5)
(Hydrocarbons) (Volatility)

DANILOV, S.N., gl^{av}. red.: ARBUZOV, A.Ye., red.; VVEDENSKIY, A.A., red.; VENUS-DANILOVA, E.D., red.; ZAKHAROVA, A.I., red.; IOFFE, I.S., red.; KAVERZNEVA, Ye.D., red.; LUTSENKO, I.F., red.; MISHCHENKO, K.P., red.; NEMTSOV, M.S., red.; PETROV, A.A., red.; FREYDLINA, R.Kh., red.; SHEMYAKIN, M.M., red.; SHUKAREV, S.A., red.; YUR'YEV, Yu.K., red.

[Biologically active compounds] Biologicheski aktivnye soedineniia. Moskva, Nauka, 1965. 305 p.
(MIRA 18:7)

BUROVA, G.V.; KOGAN, V.B.; NEMTSOV, M.S.

Liquid - vapor equilibrium in the quaternary and ternary systems formed by C₅ hydrocarbons and separating agents. Zhur. prikl. khim. 38 no.1:121-128 Ja '65.

Relation between solubility and effectiveness of separating agents used in the processes of extraction rectification. Ibid.:128-134 (MIRA 18:3)

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

BUROVA, G.V.; KOGAN, V.B.; NEMTSOV, M.S.

Liquid - vapor equilibrium in ternary systems forced by
C₅ hydrocarbons and a separation agent at elevated temperatures
under pressure. Zhur.prikl.khim. 38 no.11:2505-2513 N '65.
(MIRA 18:12)

1. Submitted November 4, 1963.

GENKIN, A.N.; BOGUSLAVSKAYA, B.I.; BRESLER, L.S.; NEMTSOV, M.S.

Determination of the thermodynamic functions of interaction of substances with polar solvents by gas-liquid chromatography.

Dokl. AN SSSR 164 no.5:1089-1092 0 '65.

(MIRA 18:10)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut neftekhimicheskikh protsessov i Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im. S.V.Lebedeva. Submitted February 2, 1965.

L 47125-66 ENT(d)/ENP(1) IJP(c) BE/CG
 ACC NR: AR6016012 SOURCE CODE: UR/0271/66/000/001/A009/A009
 INVENTOR: Nemtsov, M. V. ; Shamayev, Yu. M. 60
 B

TITLE: Investigation of the switching processes of rectangular hysteresis loop ring cores in weak magnetic fields
 SOURCE: Ref. zh. Avtomat. telemekh. i vychisl. tekhn., Abs. 1A53
 REF SOURCE: Tr. Mosk. energ. in-ta, vyp. 60, ch. 2, 1965, 87-99

TOPIC TAGS: magnetic core, hysteresis loop, magnetic permeability, magnetic viscosity, ring core, miniature core

ABSTRACT: A description is given of methods developed for investigating pulse magnetic reversal of miniature cores with a rectangular hysteresis loop in magnetic fields corresponding to the ascending sector of the full hysteresis loop. A pulse program providing for magnetic reversal along the limit cycle acts upon the core. In weak fields the viscosity processes in magnesium-manganese ferrites strongly depend on temperature. Maximum viscosity coincides with maximum permeability and is attained in the intensity region corresponding to the initiation of magnetization. The design of the measuring system is described and schematic diagrams of some of its individual units (key using type-P407 transistor, phantastron delay line) are presented. Orig. art. has: 10 illustrations and a bibliography of 4 titles. N. P. [Translation of abstract] [DW]

LS SUB CODE: 09/
 Card 1/1 UDC: 62-523:681.142.672+621.318:565

L 02308-67 ENT(1)

ACC NR: AR6016562

SOURCE CODE: UR/0196/65/000/012/BC01/B001

AUTHOR: Nemtsov, M. V.

TITLE: Dynamic surface for pulsed alternating magnetization of ferrites in a limiting hysteresis cycle

21 48
B

SOURCE: Ref. Zh. Elektrotehnika i energetika, Abs. 12B4

REF SOURCE: Tr. Mosk. energ. in-ta, vyp. 60, ch. 2, 1965, 51-54

TOPIC TAGS: hysteresis loop, magnetic hysteresis, pulsed magnetic field, ferrite

ABSTRACT: One of the methods for representing the pulse properties of ferrites is the dynamic surface which is the set of phase curves $dB/dt=f(b)$ at $H_m = \text{const}$ for transition processes during magnetic reversal of the core from the B_r state by positive square-wave current pulses. The dynamic surface is considered for pulsed alternating magnetization of K-222 ferrite ($3 \times 2 \times 1.5$ mm) with $H_c = 0.144$ a/cm, $B_r = 0.23$ stl and intersection of the surface by planes $B = \text{const}$ and $H = \text{const}$. This dynamic surface is strictly valid only for square-wave magnetizing pulses. It is shown that there is a region in direct proximity to the static hysteresis loop which is characterized by extremely slow processes (tens of msec). Ductility in fields

UDC: 621.318.13

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L 02308-67

ACC NR: AR6016562

corresponding to the ascending section of the limiting hysteresis loop is sharply dependent on temperature, a fact which is not observed in large fields. [Moscow Power Engineering Institute]. V. Glotov. [Translation of abstract]

SUB CODE: 09

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