DEAMEN, P. P.

GRANKIY, Viktor Isidorovich; BRHEZIN, B.P. nauchnyy redsktor; VOLOSHIN,
D.A., redsktor

[What the foundry worker should read; a bibliography] Chto chitet'
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Nauchnyt red. B.P.Baresin. Leningrad, Gos., sublichnets biblioteca
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N., KOTS, 1954 132 S. S. ILL. 22 SR 3000 EKZ 4 \$ 60 K
(55-2330) 334.6: 672 plus 672

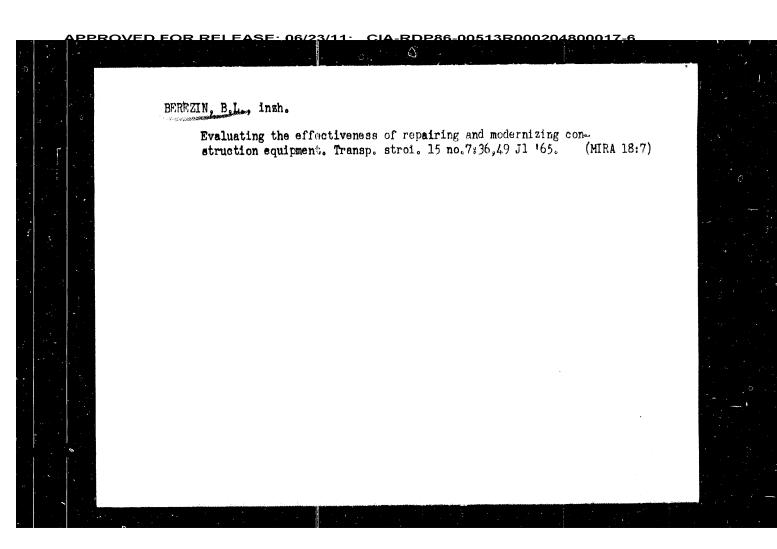
SO: KAIZHANYA METOPIS' NO. 6, 1955

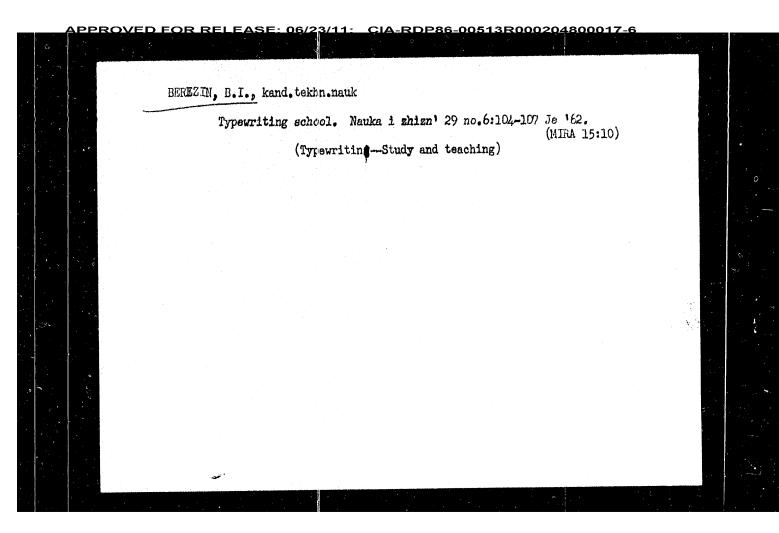
BEREZIN, B. P.

BEREZIN, Boris Mikhaylavich; PASYNKOV, V.V., prof., doktor tekhn.nsuk, otv.red.; VARRINTERATA, A.I., red.; TRAL, R.K., tekhn.red.

[Materials for electricians in shipbuilding] Materialovedenie dlis elektrikov-sudostroitelei. Leningrad, Gos.sciusnoe izd-vo sudostroit.promyshl., 1960. 212 p. (MIRA 13:5)

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ZONIS, Semen Aleksandrovich; MAZUROV, Sergey Mikhaylovich; BEREZIN,
B.I., red.; ZAKHARIKOVA, Ye.I., red.; zd-va; GARINA, T.D.,
Tekhn. red.

[Laboratory and lecture experiments and demonstration materials in organic chemistry] Laboratorno-lektsionnye cypty i demonstrationnye materialy po organicheskoi khimii. 1zd.2., ispr. i dop. Moskva, Gos. izd-vo "Vysshata shkola," 1961. 720 p.

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(Chemistry, Organic—Laboratory magnuals)

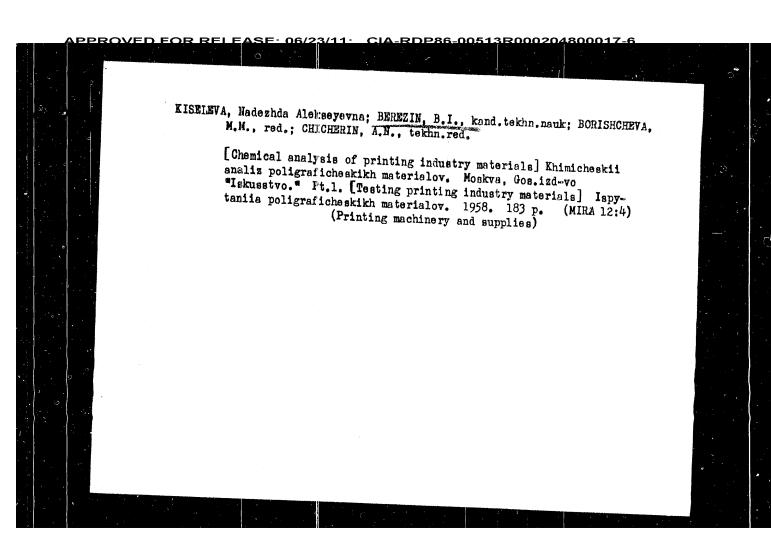
BEREZIN, Boris Ivanovich; ROMM, R.S., red.; SHPAK, Ye.G., tekhn. red. [Printing inks] Pechatnye kraski. Moskva, Gos. nauchno-tekhm. izd-vo khim. lit-ry, 1961. 215 p. (MIRA 14:11) (Printing ink) ERREZIN, B.I., otv. red.; KOZAROVITSKIY, L.A., red.; MEDVEDEV, Io.M., red.; POROVA, A.L., red.; PORTAUDKHIN, P.A., red. SMEROV, S.S., red.; SOPOVA, O.I., red.

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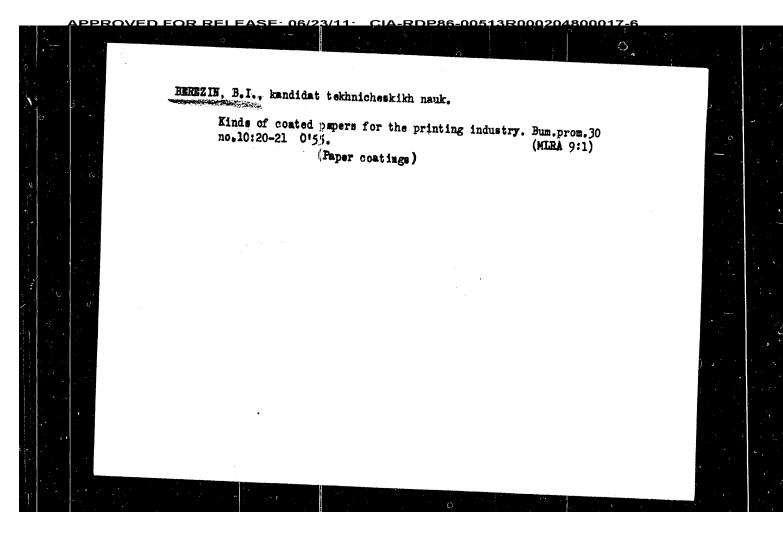
BEREZIN, B. I., kandidat tekhnicheskikh nauk.

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32 no. 4:27 lp '57.

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(MIRA 10:7)



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M.Ye.; ALEXSANTROV, V.I., tekim.red.

[Printing materials] Poligraficheskie materialy. Moskva, Gos.
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(Bookbinding-Aquipment and supplies)

BEREZIN, B.I., kandidat tekhnicheskikh nauk.

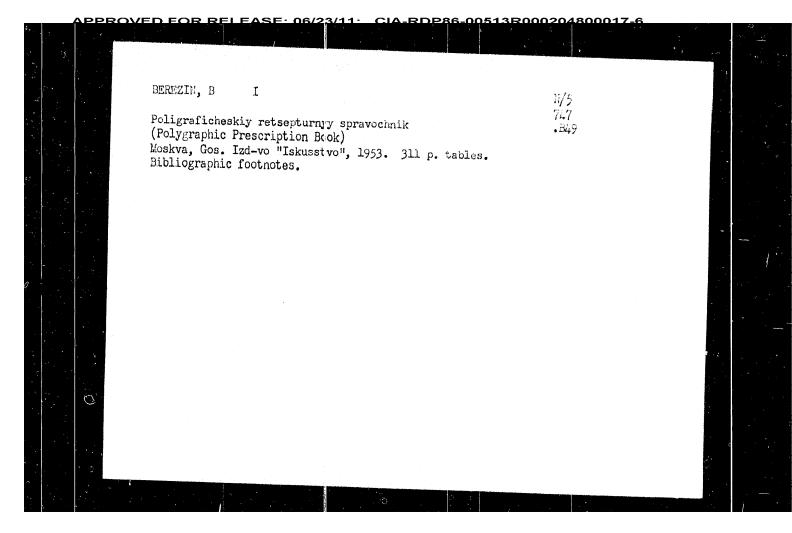
Printing properties of paper. Bun.prom. 28 no.8:12-15 Ag '53.

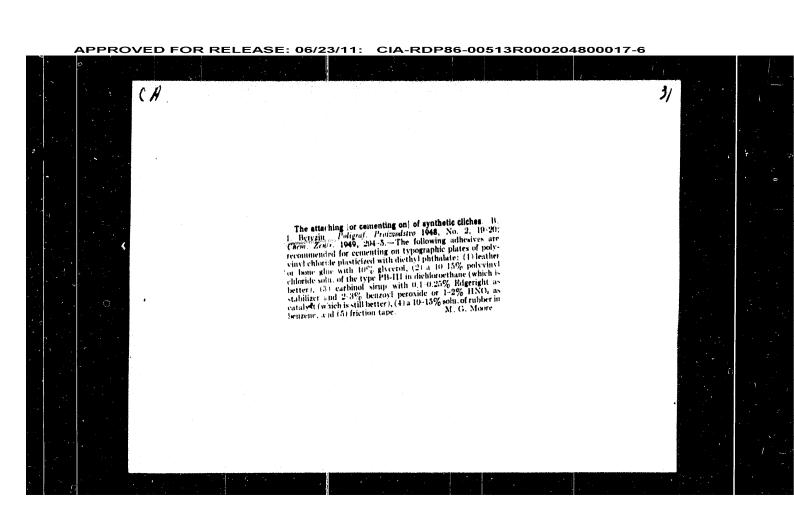
(MLRA 6:7)

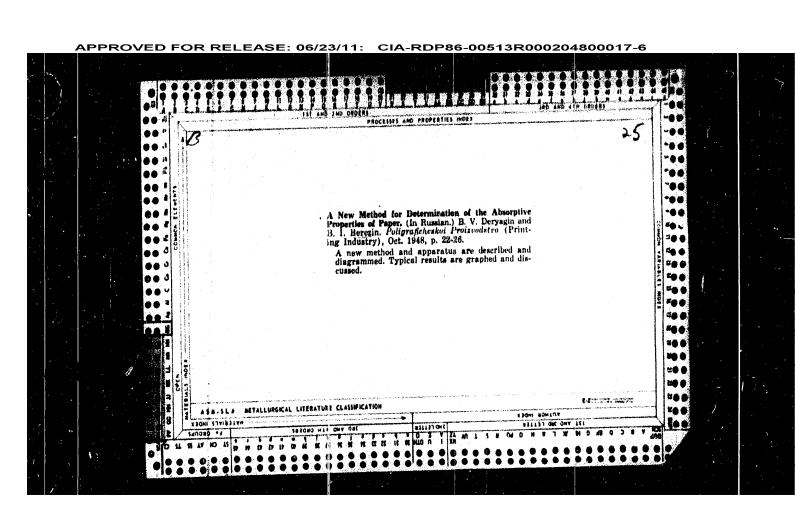
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Staining of litho-offset forms and problems concerning the theory of printing element formation. Poligr. proiz. 4:15-16 Ap '59. (MIRA 6:6) (Lithography--Metal plate processes)







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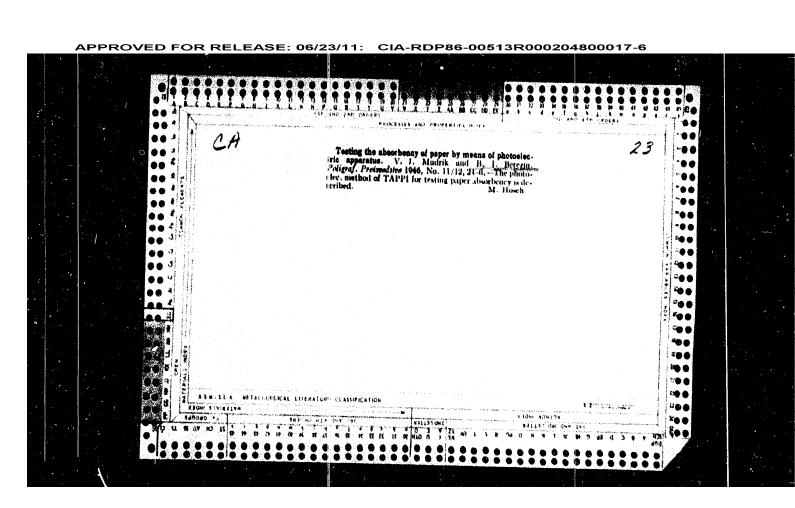
BEREZIN, B

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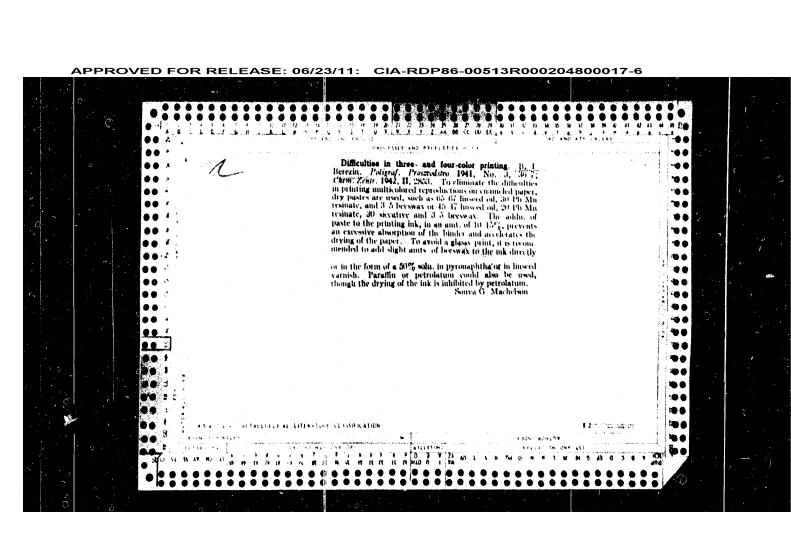
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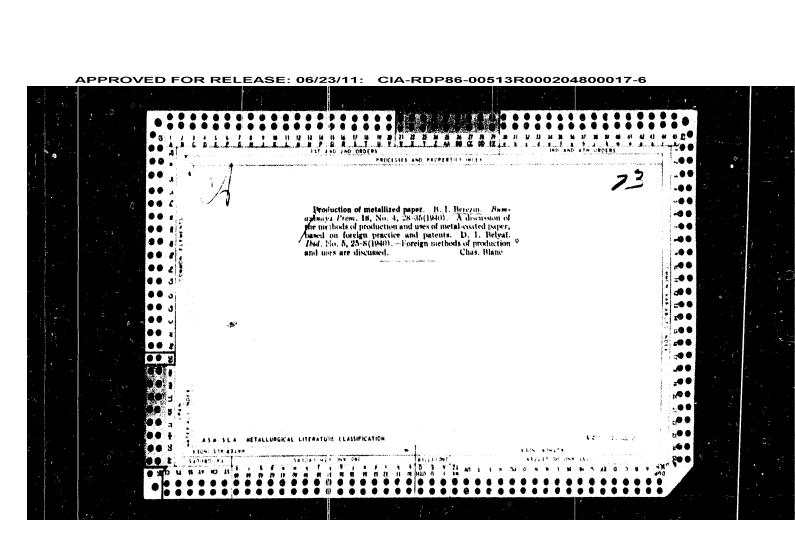
304 P. Illus., Diagrs. Bibliographies at end of chapters.

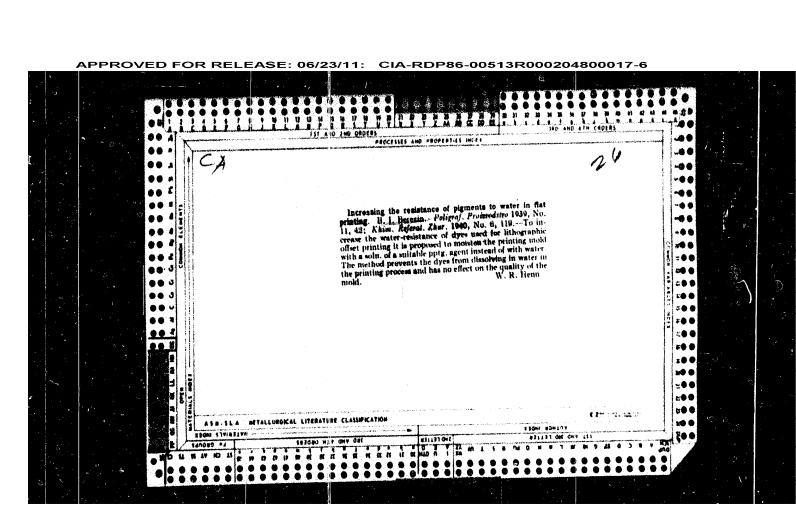
Gives information on designation, quality and working principles of Polygraphic materials, applicable for courses in studying material. used for polygraphic production.

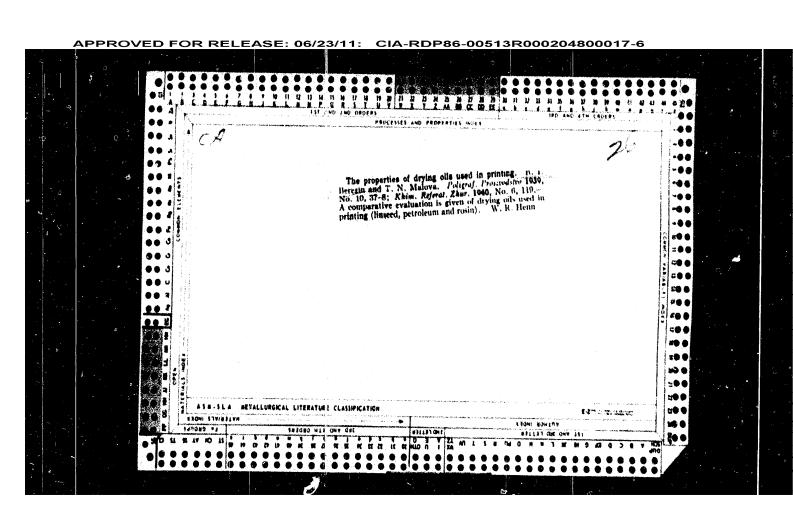


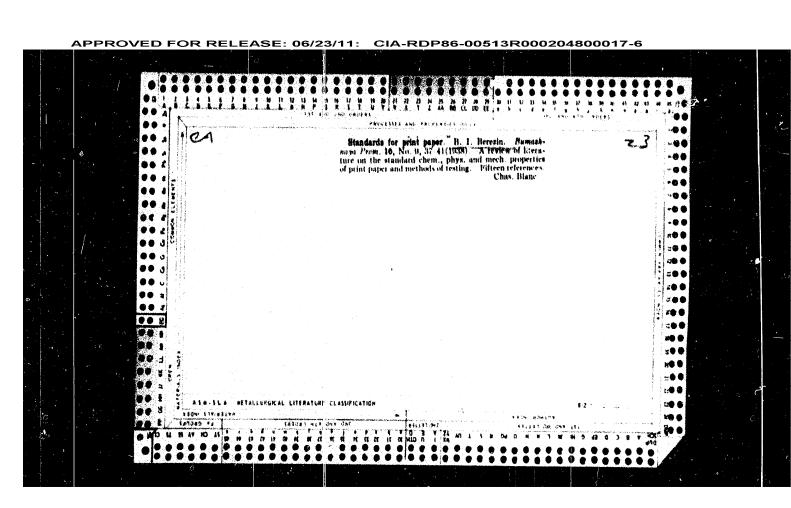
Substitute for lineard drying all J. J. Herena and S. V. Buolat. Pagestive 1966. No. Pro. 1970. September 1970

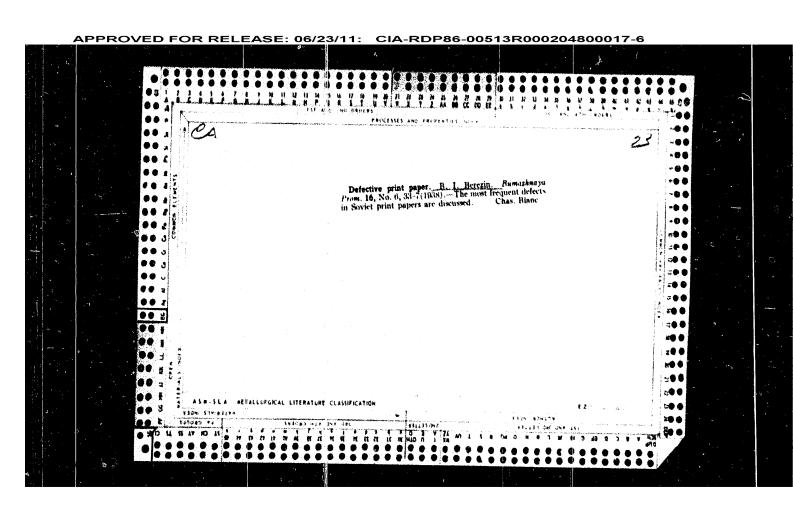




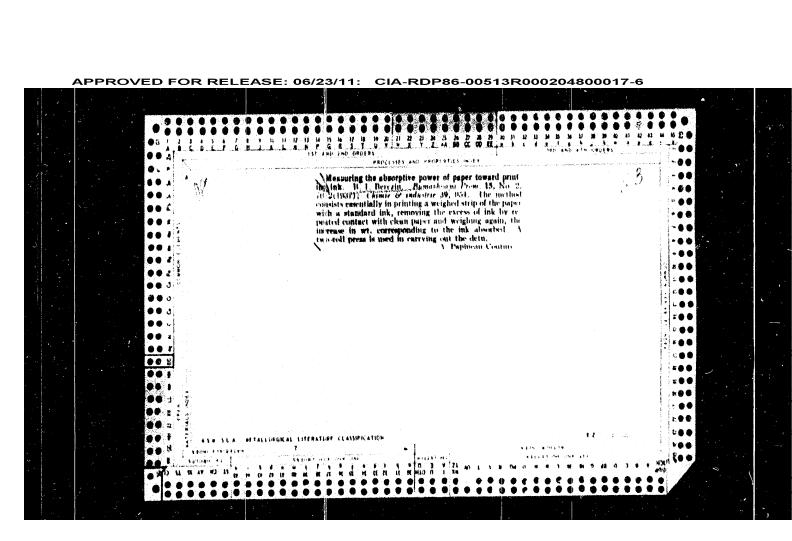


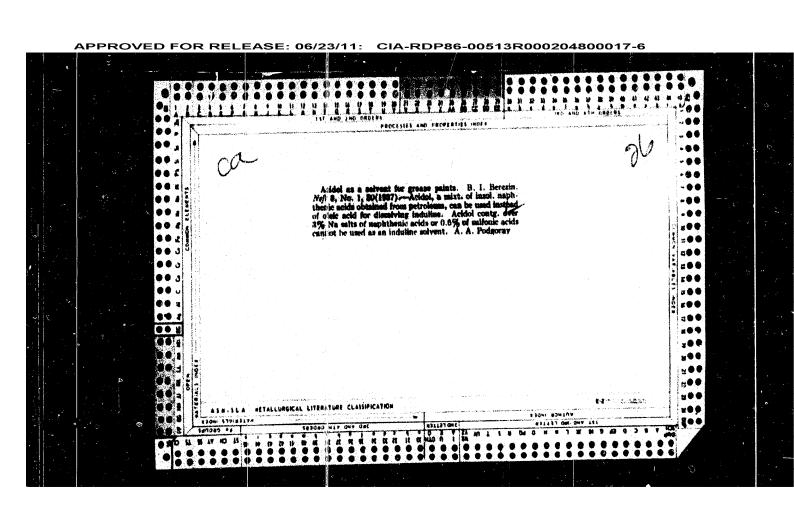


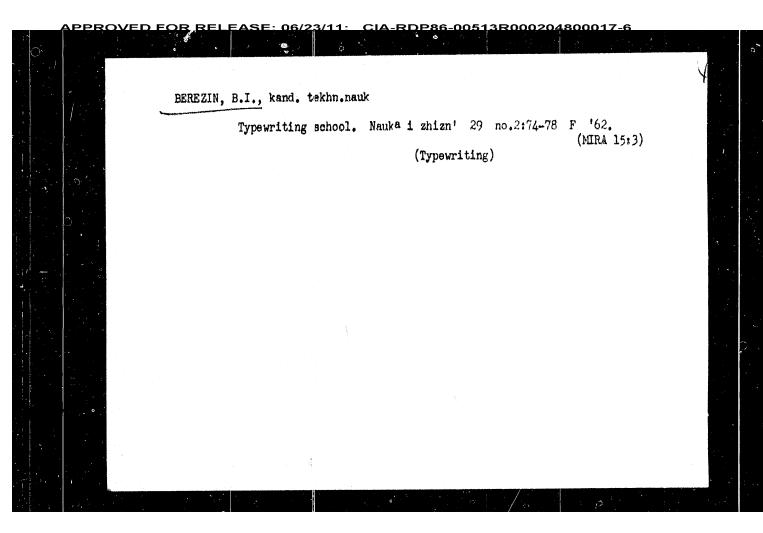


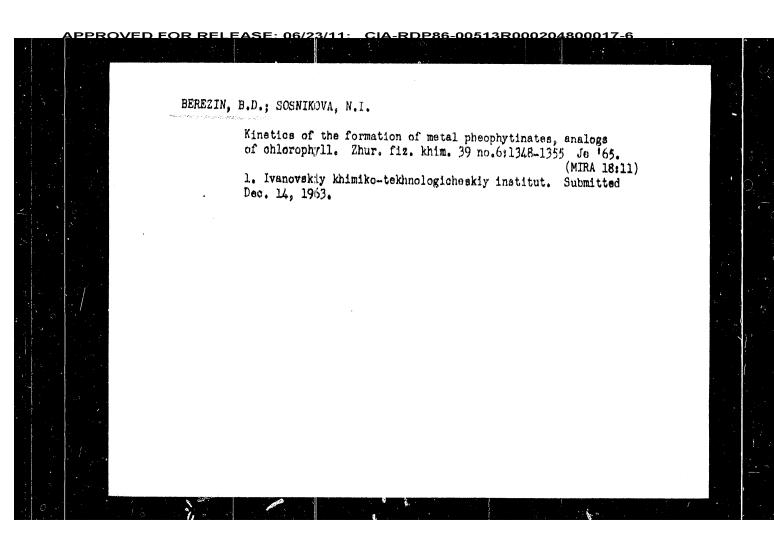


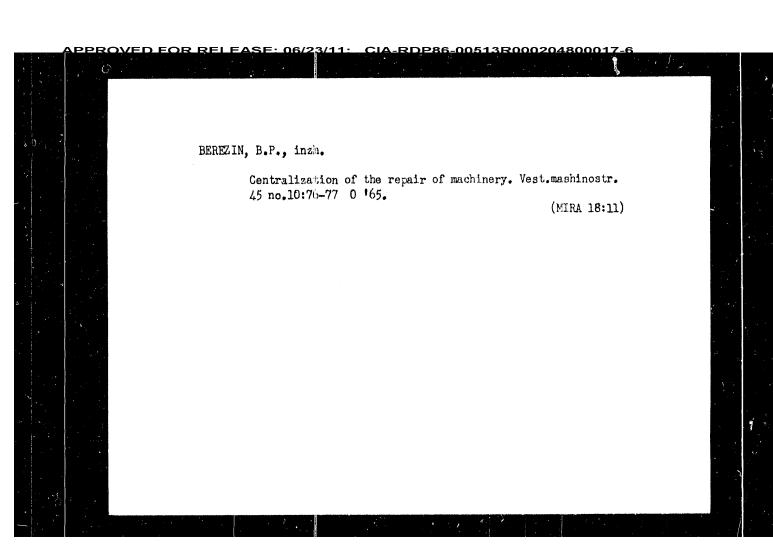
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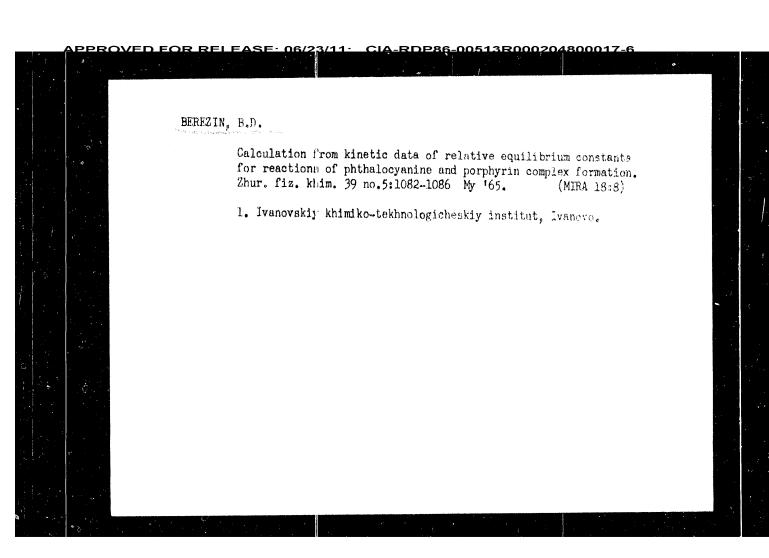


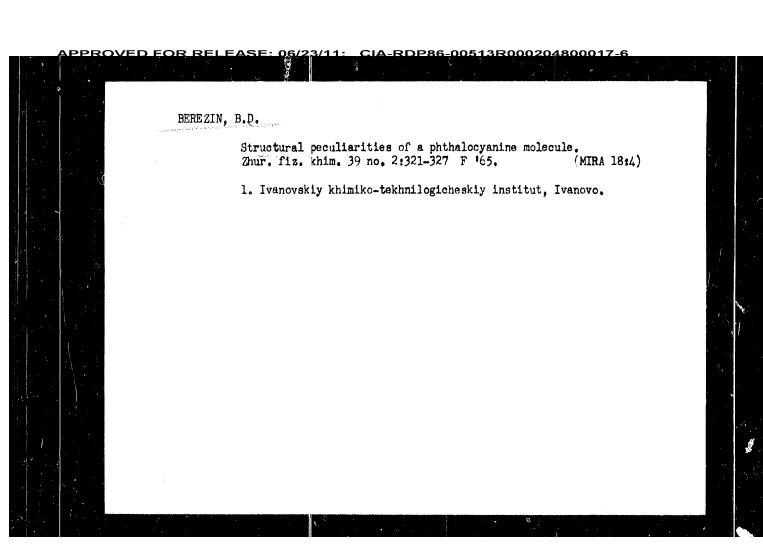




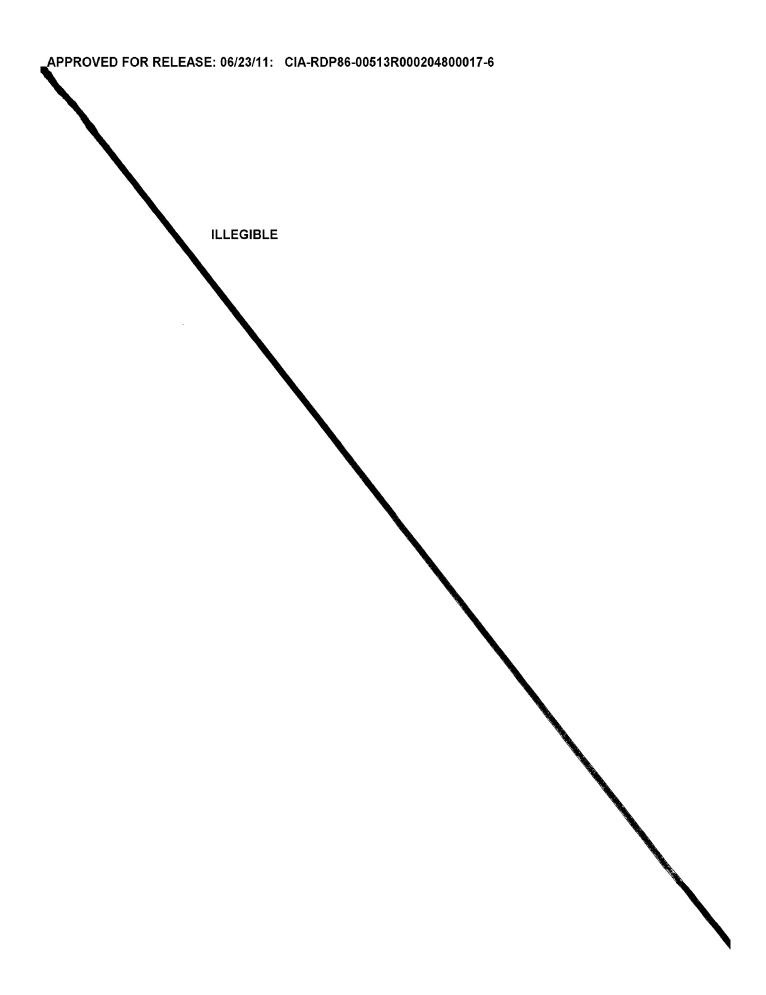


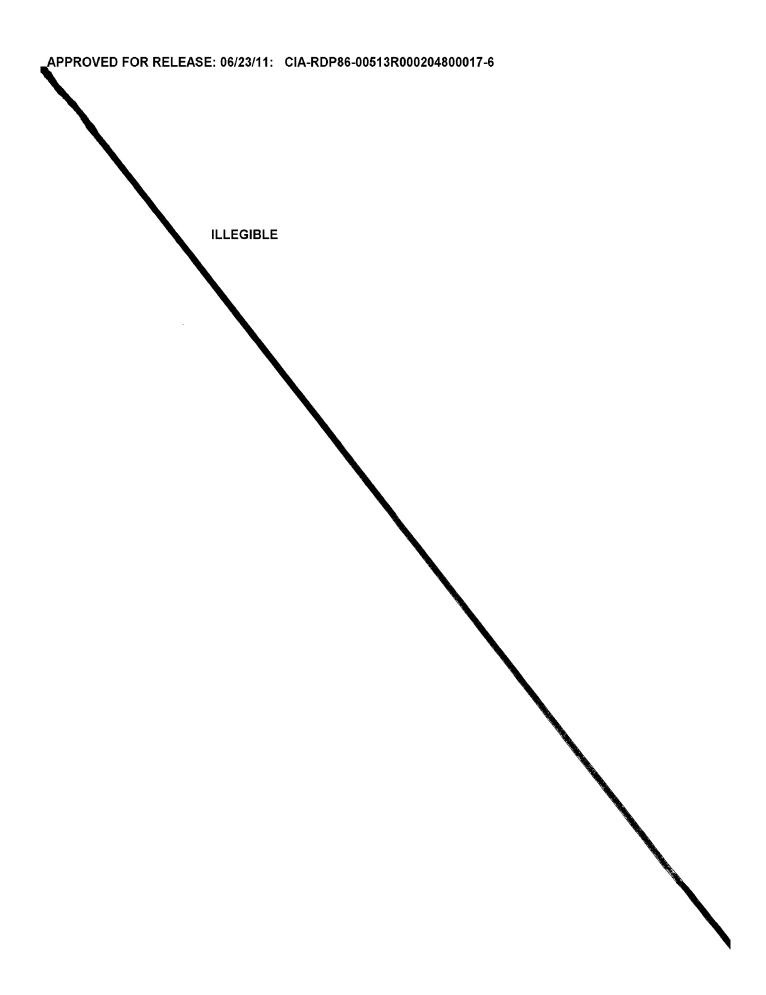


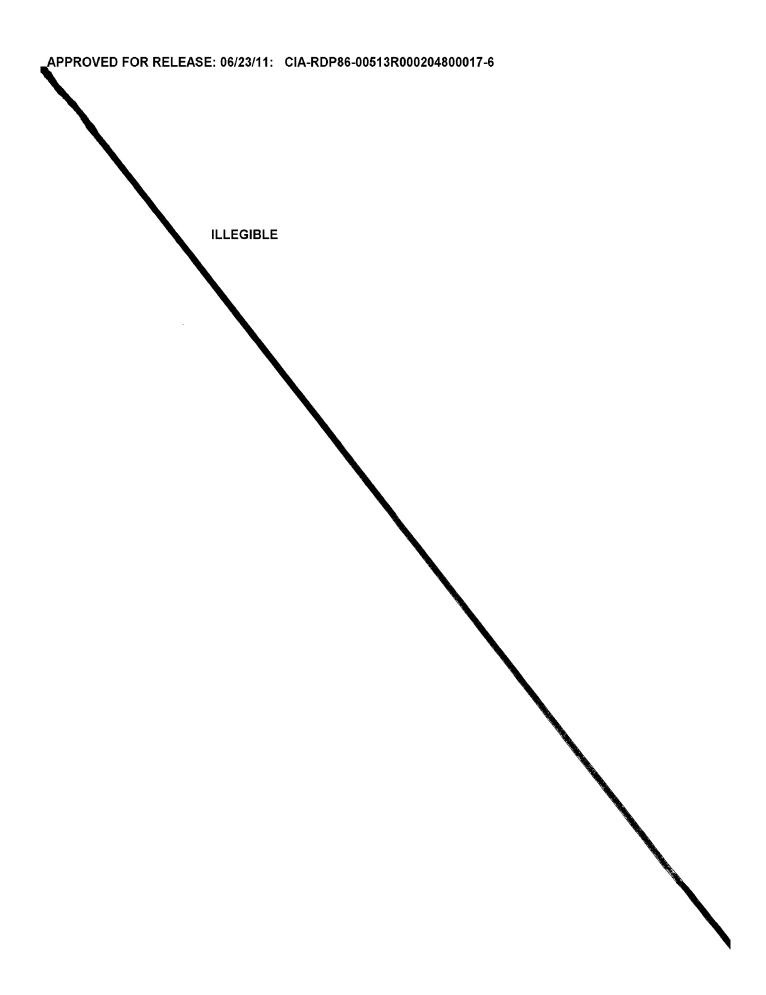




BEREZIN, B.P., SOSNIKOVA, N.I. Kinetics of the formation of metal pheophytinates, analogs of oblorophyll. Zhur. fiz. khim. 38 no.5:1216-1222 My '64. (MIRA 18:12) 1. Ivanovskay khimiko-tekhnologicheckiy institut. Submitted June 18, 1963.







BEREZIN, B.D. Interrelation between the stability and kinetic characteristics of phthalocyanire complexes. Zhur. fiz. khim. 38 no.2957-2961 D '64. (MIRA 18:2) 1. Ivanovskiy khimiko-tekhnologicheskiy institut.

APPROVED FOR RELEASE: 06/23/11: CIA-RDP86-00513R000204800017-6

ACCESSION NR: AP4034575

nature of the central atom. The dissociation of metalphthalocyanines (MPc) in aqueous proton-containing solutions is irreversible: MPcH + 2H₃O — M²_{aq} + H₂PcH . The entropy and energy of activation of this dissociation reaction were calculated. It was suggested that in the process of the trimolecular reaction the activated complex (MPcH .2H₃O +) forms from the initial MPcH and H₃O because of their strong mutual polarization. The negative values of the entropy of activation are explained by the high charge and strong polarization of the activated complex which makes it more strongly solvated than the initial particles. The special role of the H₃O as a source of H₂O molecules required for the formation of the activated complex and completion of the dissociation is pointed out. "N. I. Sosnikova took part in the experimental work."... "I thank prof. K. B. Yatsimirsk for discussion of the given work." Orig. art. has: 3 tables, 6 figures and 7 equations.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovs Chemical Tech-

SUBMITTED: 13Feb63

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ACCESSION NR: AP4034575

ACCESSION NR: AP4034575

AUTHOR: Berezin, B. D. (Ivanovo)

TITLE: The mechanism of dissociation of metalphthalocyanines

SOURCE: Zhurnal fizicheskoy khimii, v. 38, no. 4, 1964, 850-857

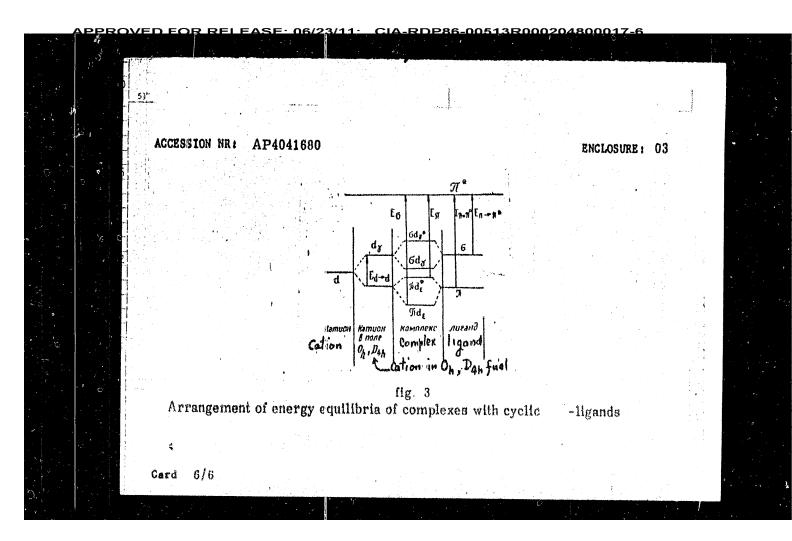
TOPIC TAGS: metal phthal-cyanine, dissociation, mechanism, dissociation rate, activation energy, activation entropy, metalphthalocyanine hydronium ion complex, trimolecular reaction

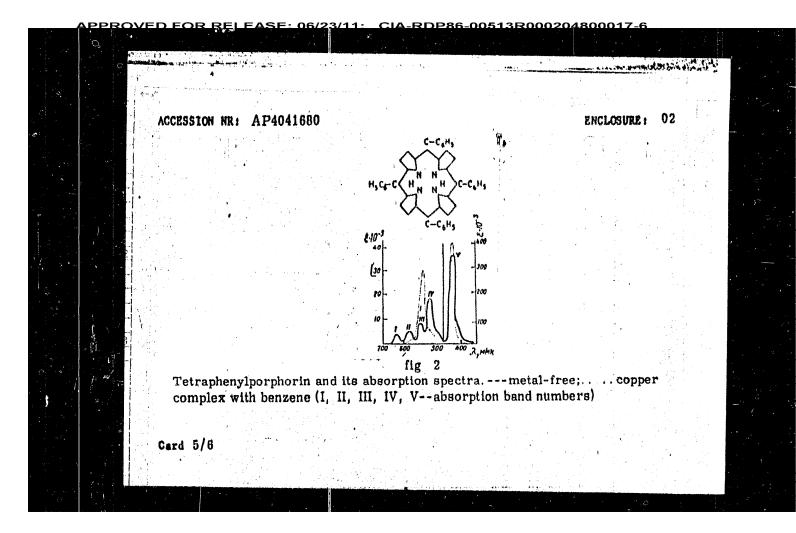
ABSTRACT: The dissociation rate of stable Co, Ni, Al, Ga, Os(IV), Rh(III) phthalocyanines in sulfuric acid solutions in the 100-160C range was investigated. The general equation

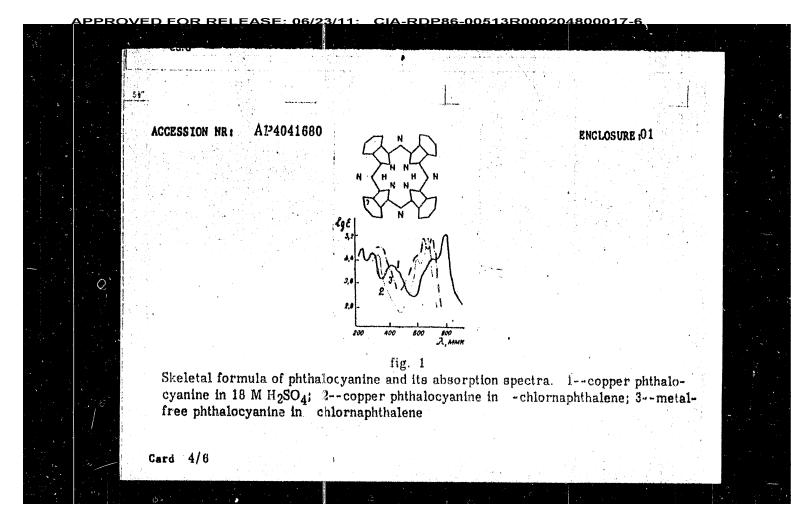
- \frac{dcupelit}{dt} = k_{\text{s}'} \text{RPCH}^{\text{c}}_{\text{In,0}},

(where check+ is the concentration of the phthalocyanine proton in solution) was found to obtain for the dissociation of the metalphthalocyanines regardless of the

BEREZIN, B.D. Synthesis and properties of gallium phthalocyanines. Izv.vys.ucheb. zav.; khim. khim. tekh. 7 no.6:982-988 164. (MIRA 18:5) 1. Ivanovskiy khimiko-tekhnologicheskiy institut, kafedra analiticheskoy khimii.







ACCESSION NR: AP4041680

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut Laboratoriya termodinamiki khimicheshikh reaktsiy (Ivanovo Chemical Technological Institute Laboratory of the Thermodynamics of Chemical Reactions)

SUBMITTED: 18May63

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OTHER: 013

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ACCESSION NR: AP4041680

remaining bands are caused by $\pi \rightarrow \pi^*$ transitions. In a series of divalent cations the short wave shift increases in proportion to the stability of the complex; the shift with tri- and tetravalent cations is still greater. However the magnitude of the hypsochromic shift does not correspond to the stability of the complex. Thus it was shown the shift of the primary absorption band of the electron spectra of the π -ligands depends not only on the strength of the σ -band but appears to be also a function of the nature and strength of the π -band, of the magnitude of the effective charge of the central ion in the complex, and of the geometric factor of the distortion of the ligand of the m-system upon coordination. All of these electronic and structural factors have a different effect on the strength of the complex and on the electronic equilibrium of the π ligand. It is therefore indicated that the spectral criterion used in foreign works (i.e., the greater strength of the complexes with organic m-ligands results in the greater hypsochromic shift) has very limited value. The energy equilibria of the complex, cation and cyclic π -ligand are shown schematically in Fig. 3. Orig. art. has: 2 tables and 5 figures.

Card 2/6

APPROVED FOR RELEASE: 06/23/11: CIA-RDP86-00513R000204800017-6

ACCESSION NR: AP4041680

\$/0153/64/007/002/0202/0208

TITLE: Electron absorption spectra and stability of monotypic com-

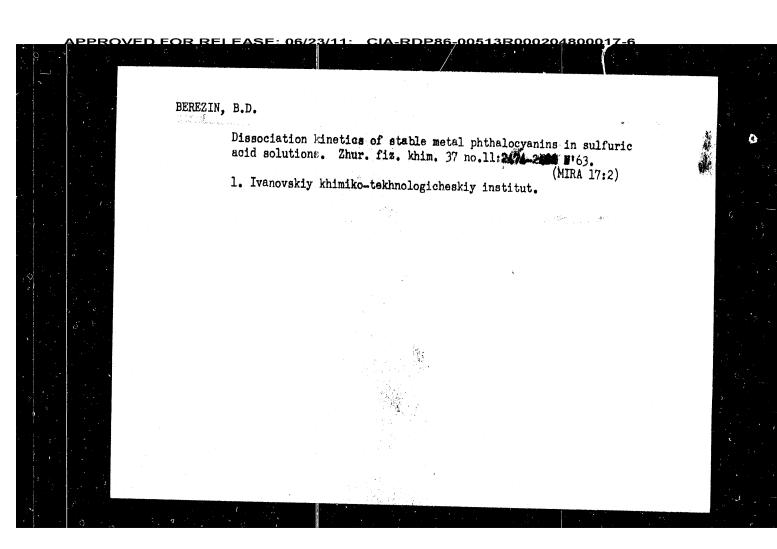
AUTHOR: Berezin, B. D.

SOURCE: IVUZ. Khimiya i khimicheskaya tekhnologiya, v. 7, no. 2, 1964, 202-208

TOPIC TAGS: electron absorption spectra, spectral band shift, cyclic pi-ligand, phthalocyanine, porphorin, coordination complex, tetraphenyl-porphorin, sigma bond strength, pi bond strength, hypsochromic shift

ABSTRACT: The relationship between the stability of complexes and the position of their absorption bands was investigated by examining in detail the shift in the absorption band in cyclic π -ligands with phthalocyanine and porphorin upon coordination with different metal ions. The shift in the long wave bands of the spectrum of phthalocyanine (Fig. 1) on complexing with Cu in α -chloronaphthalene is attributed to the π - π * transition. In α , β , ϵ , δ -tetraphenylporphin (Fig. 2) bands II and IV arecaused by π - π * transitions while the 3

BEREZIN, B.D. Physicochemical properties of phthalocyanine pigments. Part 3: Breakdown of pigment molecules in acid solutions. Chromaticity of phthalocyanines. Izv.vys.ucheb.zav.;khim. i khim. tekh., 7 no. 1:111-117 164. (MIRA 17:5) 1. Ivanovskiy khimiko-tekhnologicheskiy institut, kafedra analiticheskoy khimii.



PPROVED FOR RELEASE: 06/23/11: CIA-RDP86-00513R000204800017-6

ACCESION NR: AP4025263

1956) a theoretical analysis of the process of reprecipitation of phthalocyanine pigments (primarily in the example of CuPc) was conducted. Optimum conditions for their solution and sulfuric acid consumption required for the full solution of pigments are found. Values for sulfuric acid consumption (kilogram) needed for the total solution of 100 kg. pigment of blue phthalocyanine (calculated for pure CuPc) are given for 10 and 50 C. It follows from the data, that in the process of reprecipitation of pigment from H2SO4 solutions with less than 94% concentration only a small part of the pigment is exposed to the solution and consequently is converted into d-form; a basic part of the pigment to microcrystal degree, is in B-form. Orig. art. has: 4 tables.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanov Chemical Engineering Institute); Kafedra analiticheskoy khimii (Department of Analytical Chemistry)

SUBMITTED: 020ct62

DATE ACQ: 10Apr64

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Card 2/2

PPROVED FOR RELEASE: 06/23/11: CIA-RDP86-00513R000204800017-6

ACCESSION NR: AP4025263

8/0153/63/006/006/1016/1021

AUTHOR: Berezin, B.D.

TITLE: Physico-chemical properties of phthalocyanine pigments

2. Processes of dissolving phthalocyanines in sulfuric acid and its derivatives

SOURCE: IVUZ. Khimiya i khimicheskaya tekhnologiya, v. 6, no. 6, 1963, 1016-

TOPIC TAGS: Phthalocyanine pigment, phthalocyanine, sulfuric acid, phthalocyanine dissolution

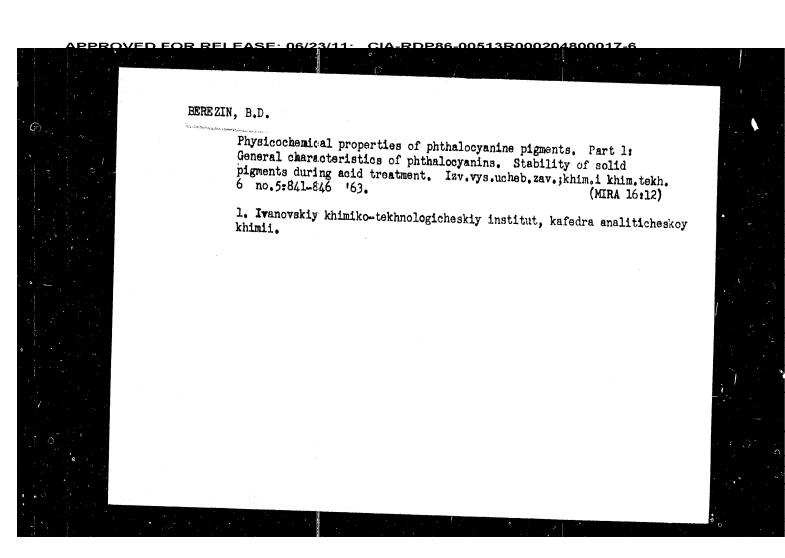
ABSTRACT: Under industrial and laboratory conditions, phthalocyanine pigments containing metal are mostly obtained using dry methods. For this purpose, the metals and their chlorides or oxides are coalesced with the phthalocyanine or with a mixture containing phthalic anhydride, urea and a catalyst. The reaction product is an extremely complex mixture. The chemical activity and thermodynamics of the reprecipitation processes of industrial fusions of phthalocyanine from solutions of sulfur, chlorosulfonic acid and fuming sulfuric acid are examined. Based on a previously given thermodynamic ration (F. Baumann et al. Angew. Chem. 68, 133,

Card 1/2

AFFEC/ASD/ESD-3 HOUSS TON BART RM/JD 8/0020/63/150/005/1039/10 AVIHOR: Berezin, B. D. TITLE: Syrthesis and properties of rhodium phthalocyanin SOURCE: AN SSSR. Doktacy , v. 150, no. 5, 1963, 1039-1042 TOPIC TAGS: synthesis, pr party, rhodium phthalocyanin, acid-stable phthalocyanin, rhodium phthalocyanin, (HS sub 4) RhPc, dissociation, equilibrium constant, Rh sup plus 3, Os sup plus 4, Pt sub plus 2, Pd sub plus 2 ABSTRACT: Supplementing estiler work of B. Berezin and N. Sosnikova (DAN, 146, 1962, 604) on soid - stable <u>phthalogyanins</u>, annydrons trivalent rhodium chlorida was reacted with a five-fol excess of phthalonitrile, with cooling for 4 hre, to form rhodium phthalocyanin; purified from acetone and from 90% H sub 2 50 sub 4, the complex (HSO sub 4) Rh to was formed. Solubility was determined and dissociation and equilibrius constants were calculated for Rh sup plus 3, Os sup plus 4, Pt sup plus 2, Pd s p plus 2, Cu sup plus 2, and Al sup plus 3 phthalocyanins. The effect ve ion charges and character of the chemical bonds in the Rh and Os complexes are discussed extensively. Absorption spectra of Rh, Os, and Pd phthalocyanin are compared. The article was presented by Academician A. K. Association; Ivanov Inst. of Chemical Technology Card 1/21

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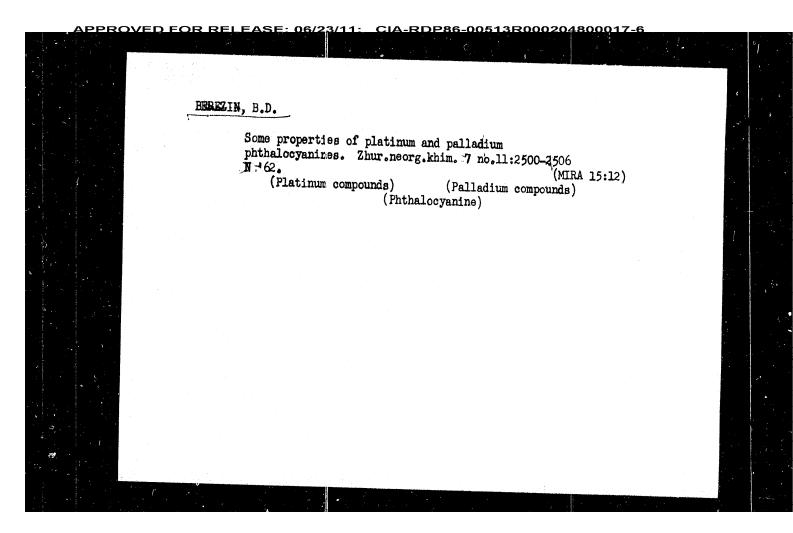
ADV/GO BEST/COP/G)/ADVIGO/ADDE Pe-11/Pr-14/Po-14/Ps-14 * DE/RM/ AN ALL COR AREA PERFORMS 8/0080/65/056/006/0181/1186 TURNOR: Parente il fi DIVINE. Solubility of pht salosymmines in chlorosulformic acid and oleum SOURCE: Commel printed by khimii, v. 36, no. 6, 1963, 1181-1186 TOPIO MAGS: por locamin ; clama, chlorosulfonio acid ABSTRACT: The application of thermodynamic data obtained from the study of phthalecyanine behavior in suits in said and also the functional properties of the soid-ity in the concentrated solutions of strong soids; permit the calculations of the solubility equilibrium of philalocyanines in chlorosulfonic soid and oleus. It also evaluates the magnitude of solubility of phtalogyanines. From the experimentel date it can be conclused that the solubility equilibrium of phthalocyanine in HOSO_cl is extremely large. In a 30% solution of oblorosulfonicacid its solubility is practically unlimiteds. At low concentrations of HOSO_Cl its solubility is limited. Thus, the corpentration of HOSOgCl approximately determines the solu untility of phthalographie. This is especially true in the case of cleue since the acidity of the media surtaining ReSpo. is much higher than the media containing HoSo_col. It is possible that the solubility in HoSo_col and cleum will be



BEREZIN, B.D.; SOSNIKOVA, N.I. Synthesis and properties of osmium phthalocyanine. Dokl. AN SSSR 146 no.3:604-607 S 162. (MIRA 15:10) 1. Ivanovskiy khimiko-tekhnologicheskiy institut. Predstavleno akademikom A.N.Tereninym. (Osmium compounds) (Phthalocyanine)

Thermodynamic characteristics of phthalocyanines in sulfuric acid solutions. Zhur.neorg.khim. 7 no.11:2507-2513
N '62. (MIRA 15:12)

1. Ivanovskiy khimiko-tekhnologicheskiy institut.
(Phthalocyanine) (Sulfuric acid) (Solubility)



Study of metal ...

S/076/62/036/003/003/011 B101/B108

by W. Caughey, A. Corwin (see below) about the mechanism of decomposition of metallic ethioporphyrine complexes are called erroneous. There are 7 figures, 3 tables, and 9 references: 4Soviet and 5 non-Soviet. The four most recent references to English-language publications read as follows: W. Caughey, A. Corwin, J. Amer. Chem. Soc., 77, 1509, 1955; P. Barrett,
D. Frye, R. Linstead, J. Chem. Soc., 1157, 1938; J. Anderson, E. Bradbrook,
D. Chem. Soc., 1151, 1938; P. Barrett, R. Linstead,
D. Chem. Soc., 1151, 1938; P. Barrett, R. Linstead,

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Insti-

SUBMITTED: May 25, 1960

Card 3/3

Study of metal ...

S/076/62/036/003/003/011 B101/B108

hour) at room temperature even in diluted H_2SO_4 . The unstable MPc's had constants of hydrolyzation rate different from that of H_2Pc (0.137±0.008 per hour) by one order of magnitude. Unlike the unstable MPc's whose spectra show only the absorption bands of HePcH⁺, the stable MPc's displayed absorption bands of their own. Hydrolysis proceeds as MPc's displayed absorption bands of their own. Hydrolysis proceeds as MPc's $H_2SO_4 \stackrel{\sim}{\rightarrow} MPcH^+$ $H_2SO_4 \stackrel{\sim}{\rightarrow} MPcH^+$ H_2PcH^+ (3); H_2PcH^+ $H_2PO_4 \stackrel{\sim}{\rightarrow} MPcH^+$ decomposition products (4). For stable MPc's, the reaction (3) is limiting, which proceeds according to $-dc_{MPc}/dt \stackrel{\sim}{\rightarrow} k_{MPc}c_{MPc}c_{H30} \stackrel{\sim}{\rightarrow} k_{MPc}$, while for the unstable MPc's, the reaction (3) proceeds rapidly and the reaction (4) slowly. For that group the kinetic equation as found for H_2Pc is $-dc_{MPc}/dt$ $-k_{H2Pc}c_{MPc}c_{H30} \stackrel{\sim}{\rightarrow} k_{D}c_{MPc} \stackrel{\sim}{\rightarrow} k_{D}c_{MPc}$

S/076/62/036/003/003/011 B101/B108

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AUTHOR:

Berezin, B. D.

TITLE:

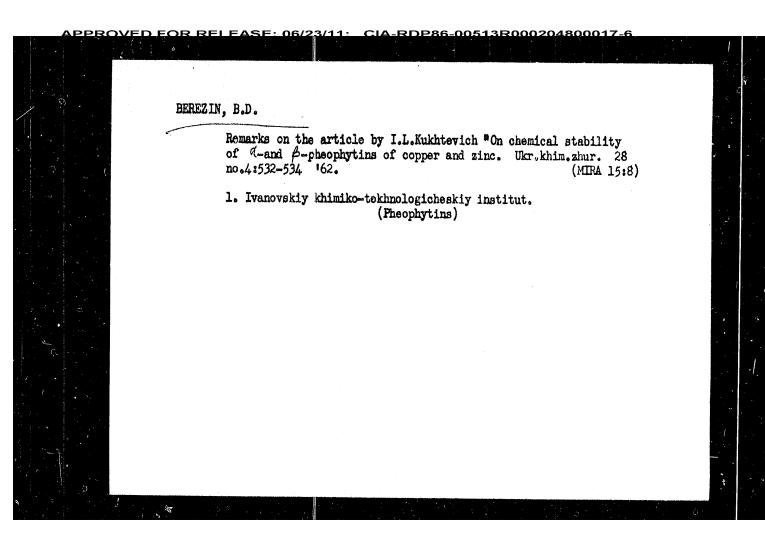
Study of metal phthalocyanines in solution. VI. Effect of the nature of the central ion on the strength of the phthalocyanine macro-ring in sulfuric acid solutions

PERIODICAL:

Zhurnal fizicheskoy khimii, v. 36, no. 3, 1962, 494 - 501

TEXT: The stability of the compounds MPc of phthalocyanine (H₂Pc) with cu^{2+} , Ni^{2+} , co^{2+} , Zn^{2+} , Sn^{2+} , Sn^{4+} , $A1^{3+}$, $V0^{2+}$, Cd^{2+} , Pb^{2+} , Mg^{2+} , Ag^{4+} , Fe^{3+} as well as of the chlorinated compounds Cl_{15} PcCu in 12 - 17.7 mole/liter H_2SO_4 was investigated at 25 - 65°C. The compounds can be divided into two groups: (1) stable compounds of Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , $A1^{3+}$, $V0^{2+}$, which displayed no noticeable dissociation at room temperature, (2) unstable compounds of Mg^{2+} , Cd^{2+} , Ag^{4+} , Pb^{2+} , Fe^{3+} , Sn^{2+} , Sn^{4+} . The stable MPc's and Cl_{15} PcCu had very small constants of hydrolyzation rate (k~10-4 per

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Methods of investigating ...

Ref. 7: R. Williams, Chem. Revs, 56, 299 (1956); Ref. 10: W. Caughey, A. Corwin, J. Am. Chem. Soc., 77, 1509 (1955); Ref. 16: N. Deno, R. Taft, J. Am. Chem. Soc. 76, 244 (1954).

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Institute of Chemical Technology)

PRESENTED: June 23, 1961, by A. N. Terenin, Academician

SUBMITTED: June 22, 1961

Table 1. pK of the equilibrium constants of reaction (3) of stable phthalocyanins at 25° C.

Legend: (1) Phthalocyanin.

Table 2. Temperature dependence of pK of phthalocyanins in H_2SO_4 .

Legend: (1) Temperature, OC; (2) pK of phthalocyanins of metals.

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Methods of investigating ...

the same manner as free Pc. The hydrolysis of H_2PcH^+ is complicated. The hydrolysis mechanism of stable MPc was studied with the most unstable MPc: $(HSO_4)_2SnPc$. The hydrolysis also follows the equation $MA_n \rightarrow M^{H^+} + nA^-$ (1). The limiting stage in unstable Pc, however, is the hydrolysis of the H_2PcH^+ macroring, whereas in stable MPc it is the metal separation (2a). Thus, four coordinate bonds between metal and nitrogen are ruptured. The hydrolysis of stable Pc is only noticeable, at 100 - 120°C. As to the readiness of separation of the central ion in Pc, the metals form the order $V^{4+} > Zn^{2+} > cu^{2+} > Co^{2+} > Ni^{2+} > Pt^{2+}$. At the same time, the basic properties of the four N atoms of the rings participating in (2) and (2a) are increasingly neutralized. Pt has the highest stability, but also (HSO_4) AlPc is very stable. The above order reflects the stability order in porphyrin complexes: Ba $^{2+} > Mg^{2+} > Mn^{2+} > Fe^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Pd^{2+}$. There are 6 tables and 18 references: 12 Soviet and 6 non-Soviet. The three references to English-language publications read as follows:

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Methods of investigating ...

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Since the constants remain unchanged at all temperatures, concentrated HoSO, is an ideal solvent. Thus, the ratio of activity coefficients of the reactants in (3) also remains constant, and the reaction product, (MPcH)HSO $_4$, is completely dissociated. MPcH $^+$ predominates in sulfuric acid solutions. The equilibrium constants pK of reaction (3) allow conclusions as to the formation and durability of σ - and π -bonds, the stability of MPc, the existence of an excessive charge on the central ion, and the induction effect of the substituents in the benzene ring. The effect observed is an endothermic one which decreases with increasing solvation ability of Pc, either because of the ability of additional coordination of the central ion (ZnPc, ZnPcCl), or due to a charge of the central ion ($^+$ AlPcCl), or the polarization of bonds in the chlorination of benzene rings (CuPcCl $_{15}$). Pc disintegrates in sulfuric acid solutions and is completely hydrolyzed on the macroring. $\begin{bmatrix} \text{H}_2(\text{C}_8\text{H}_4\text{N}_2)_4\text{H}^+ \end{bmatrix} + 8\text{H}_2\text{O} + 3\text{H}^+ \longrightarrow 4\text{C}_8\text{H}_5\text{O}_2\text{N} + 4\text{NH}_4^+ + \text{H}_2\text{.} \\ \text{MPcH}^+ \text{ and } \text{H}_2\text{PcH}^+ \text{ disappears.} \\ \text{All unstable Pc were found to hydrolyze in}$

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Methods of investigating ...

of stable Po formed by Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Pt^{2+} , Pd^{2+} , V^{4+} , $AlCl^{2+}$, and partly $SnCl^{2+}_2$, according to Eqs. (2) and (2a) is hardly noticeable. In aqueous, acid media, stable Po disposints approximately according to

In aqueous, acid media, stable Pc dissociate irreversibly according to (2) and (2a). Despite a marked ionic dissociation in acid media, Pc cannot be characterized by the equilibrium constant of (2) or (2a). In those cases where it is difficult or impossible to determine the instability constant, or where the binding emergy between metal and addenda cannot be measured, it is possible to apply, among others, the method of determining the rate of metal separation under the action of acids (Ref. 10, see below). This method was tested on Pc complexes. The forms of Fr existence in $\rm H_2SO_4$

at various temperatures, and the properties of $\rm H_2SO_4$ as solvent were studied in preliminary experiments. In an earlier study (Knim. i khim. tekhnol. 2, 165 (1959): 4, 45, 379 (1961)) the author proved that Po in concentrated $\rm H_2SO_4$ at normal temperatures behaved like momental bases:

 $MPc_s + H_2SO_4 \xrightarrow{\longrightarrow} MPcH^+ + H_2SO_4^-$ (3). Table i gives equilibrium constants of Eq. (3) at 25°C. Those of industrially important Pc are given in Table 2.

Card 2/6 5

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AUTHOR:

Berezin, B. D.

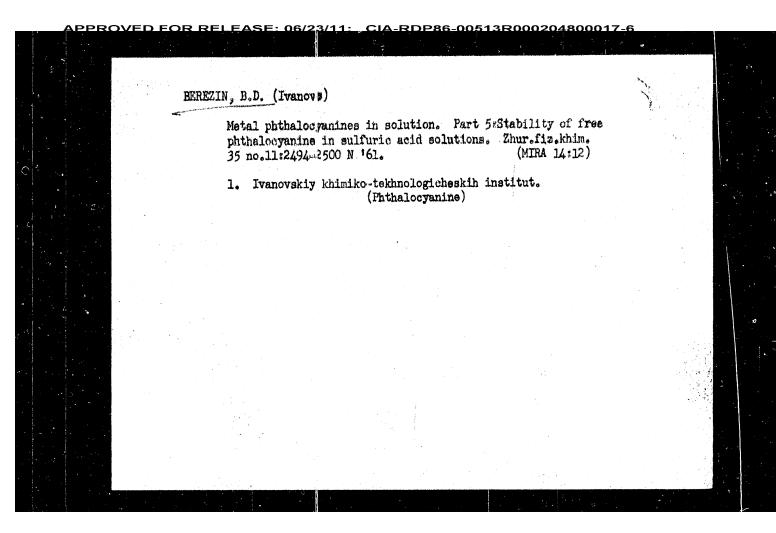
TITLES

Methods of investigating the statility of phthalocyanine complex compounds

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 141, no. 2, 1961, 353-356

TEXT: The dissociation of metal phthalocyanines which is only noteworthy in proton acid media was studied in this paper: MPC + 2H = M²⁺ + H₂PC (2); MPoH + 2H = H₂PCH + M²⁺ (2a), where PC is the bivalent anion of tetrabenzo tetrazaporphin (phthalocyanine), and M²⁺ is a metal ion. Process (2) takes place in solid phase, and (2a) in H₂SO₄ with a concentration of more than 8 moles/liter. Processes (2) and (2a) were found to be fast and irreversible with unstable phthalocyanines. 1. e., with those formed by cations of alkalis, alkaline earths, Hg²⁺, Cd²⁺, Pb²⁺, Mg²⁺, Be²⁺, Ag⁺, Fe²⁺, and those containing Sb³⁺, Mn²⁺, and Sn²⁺. The conversion

Card 1/8 4



A study of metal phthelocyanines ... S/076/61/035/011/005/013
B140/B147
Chem. Reve., 16, 67, 1935; W. Caughey, A. Corvin, J. Amer. Chem. Soc., 77, 1509, 1955.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Institute of Chemical Technology)
SUBMITTED: March 16, 1960

A study of metal phthalocyanines ... S/076/61/035/011/005/013 B140/B147 calculated and found to be $1.12 \cdot 10^{-4}$ hr⁻¹ which inserted in Eq. (2) yields $-\frac{d[H_2P_G]}{dt} = 1.12 \cdot 10^{-4} c_{H_2P_G} c_{H_3}^4 + (6)$. Reaction (4), in which 4 protons participate, is assumed to involve the shifting of 2 electrons from the H₂Pc macroring to 2 protons with evolution of H₂ gas. The hydrolytic decomposition of H₂Pc is not affected by 0₂ or light. At H₂SO₄ \leq 16 moles the rate of solution of H₂Pc is smaller than the rate of hydrolysis so that the reaction does not reach equilibrium state. At H₂SO₄ \geq 17 moles the rate of hydrolysis is smaller so that an equilibrium is reached after 1 - 2 hr. It may therefore be assumed that in 17 - 18.8 M H₂SO₄ \leq H₂PcH + HSO₄ is given by - $\log \left(\frac{H_2P_C}{H_2}\right)H_2SO_4 = 1.67 + \frac{H_2}{O}$ +8.56. N. I. Sosnikova assisted in the experiments. There are 4 figures, 2 tables, and 11 references: 5 Soviet and 6 non-Soviet. The three most recent references to English-language publications read as follows: P. Barrett, C. Dent, R. Linstead, J. Chem. Soc., 1719, 1936; L. Hammett, Card 4/5

A study of metal phthallocyanines ...

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the same way as the demomposition of ${\rm H_2Pc}$. According to Hammett, the ${\rm H_3O}^+$ concentration may be calculated as follows:

H₀ = const + $\log \frac{\text{HSO}_4}{\text{H}_2\text{SO}_4}$ (3), where const = -8.56. It was found experimentally that the H₃0⁴ concentration and k_r pass through a maximum at an H₂SO₄ concentration of 14 - 14.5 moles. The author assumes the reaction H₂PcH⁺ + 3H⁺ $\leq |\text{H}_2\text{PoH}_4|^{4+}$. Continuous uptake of H⁺ leads to rupture of the macroring which in turn results in further hydrolytic decomposition of the H₂Pc: $\left[(c_8 \text{H}_4 \text{N}_2)_4 \text{H}_6 \right]^{4+} \frac{8 \text{H}_2 \text{O}}{4} + \frac{8 \text{H}_2 \text{O}}{8} + \frac{1}{8} + \frac{1}{$

A study of metal phthalocyanines ...

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tion. The decomposition of H_2 Pc in acid solution yields the same products as are obtained by its exidation (phthalimide and ammonium salts). The influence of atmospheric oxygen and light (using a 1000 w bulb) on the decomposition rate of H_2 Pc was also studied. Evaluation of the measurement results showed that the decomposition rate of H_2 Pc increases with increasing H_2 SO₄ concentration up to a maximum and then decreases rapidly. A 17.65 M H_2 SO₄ solution still gave a distinct H_2 Pc spectrum. Graphic evaluation yielded the linear function $\log(c_0/c) = f(t)$, (t = time), where c_0 denotes the initial H_2 Pc concentration, and c the concentration in the course of the reaction. Therefore this function follows the kinetic equation $-(dc/dt) = k_c c_2$ Pc (2), where $k_r = hydrolysis$ rate constant. The characteristic decomposition reaction of H_2 Pc in H_2 SO₄ is assumed to involve the participation of H_3 O⁺, since the H_3 O⁺ concentration changes in Card 2/5

S/076/61/035/011/005/013 B140/B147

AUTHOR:

Berezin, B. D.

TITLE:

A study of metal phthalocyanines in solution. V. The stability of free phthalocyanine in sulfuric acid solutions

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 11, 1961, 2494 - 2499

TEXT: The stability of free phthalocyanine (H_2Pc) in H_2SO_4 solution was studied. Experimental procedure: Free H_2Pc is prepared by treating Na_2Pc with 96% H_2SO_4 and introducing the mixture into an ice-bath prepared from distilled water. To remove impurities, H_2Pc was heated with acetone. The stability of the H_2Pc macroring was studied using weighed portions of H_2Pc and various H_2SO_4 concentrations. The optical density of the solutions was measured at regular intervals on a KM(KM) spectrophotometer $(\lambda = 520 \text{ mm})$. 12.5 - 17.65 M H_2SO_4 solutions were used for the investigation of $(\lambda = 520 \text{ mm})$.

Study of the stability of ...

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author studied the isotopic exchange of ${\rm Co}^{2+}$ -60 with Pc of Go, Hi, Engand Al dissolved in 17.20 moles of ${\rm H_2SO}_4$ following the equations ${\rm MPcH}^+ + 2{\rm H}^+ = {\rm H_2PcH}^+ + {\rm M}^{2+}$ (2a) and ${\rm H_2PcH}^+ + {\rm Co}^{2+} = {\rm Co}^{2+$

ASSOCIATION: Ivanovsk:y khimiko-tekhnologicheskiy institut Kafedra analiticheskoy khimii (Ivanovo Institute of Chemical Technology, Department of Analytical Chemistry)

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Study of the stability of ...

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activity of the solution was determined (Table 3). Irreversibility of (1) in acid aqueous solutions may be assumed on the basis of examinations by the usual solubility method of the dissociation of less stable for of Mg, Ca, Cd, Hg, Ag, Pb, and Fe. Even with the stable compound ClFeFc, complete "washing out" of the metal with 1 mole of acid occurred after 8 - 10 days, with MgPc and PbPc it occurred after 40 - 50 hr, with AgHFc after 120 hr, with HgPs and CdPs after 12 - 15 hr, and with CaPs after 2 - 3 hr. The rate of washing depends on the type of central ion. It increases as the acid concentration increases, but it is quantitatively independent of the H ion concentration. It probably depends on the different rates of rupture of the donor - acceptor bond between metal and addendum. Presumably, it is the higher the lower the covalent character of the metal - addendum bond. It is due to residual basic properties of inner-cyclic N atoms of the macro-ring, since the basic properties of the addendum decrease as the firmness of the $\mathcal G$ -bond of metal - nitrogen increases. As regards filling of the hybrid orbit of the metal ion by electron pairs of nitrogen, the following sequences of bond firmness are given: Fe³⁺ \rangle Ag⁺ \rangle Mg²⁺, Pb²⁺ \rangle Cd²⁺, Hg²⁺ \rangle Ca²⁺. The Card 3/14

Study of the stability of ...

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of Be²⁺ from MPc proceeded more slowly than that of Mg^{2+} and other ions of less stable Pc except for Fe^{3+} , since the rates of its hydrolysis at 25°C in 17.70 and 15.40 moles of H_2SO_4 are 0.095 ± 0.008 hr⁻¹ and 1.40 ± 0.06 hr⁻¹, respectively. To study the stability of stable Po. Mos and ZhPc were formed from an alcoholic anhydrous solution of Godageov. ZnGl₂-65, and Li Pc in absolute alcohol. They were mixed by shaking with equal amounts of titrated H_2SO_4 (1 - 8 moles/liter), at 25 or 50°C and the activity of the solution was determined after centrifuging. The activity of the deposit was-20,000 pulses/min. A known volume of a Co^{0C} salv dissolved in H_2SO_4 of the same concentration (17.20 moles/liter) was added to sulfuric Pc solutions of Al, Co, Ni, and Zn contained in a bulb. Hydrolysis was conducted according to MPcH⁺ + $\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+$ + MPc and the hydrolysis was conducted according to MPcH⁺ + $\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+$ + MPc and the

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AUTHOR:

Berezin, B. D.

TITLE:

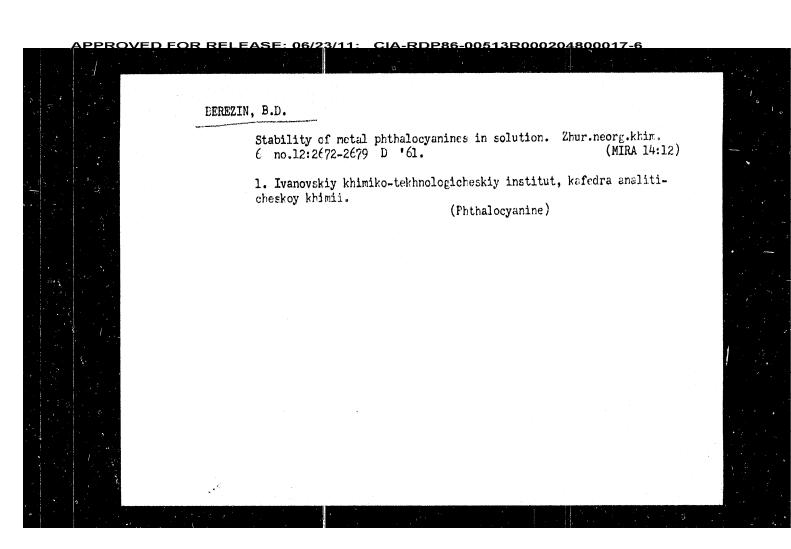
Study of the stability of phthalocyanines of metals in

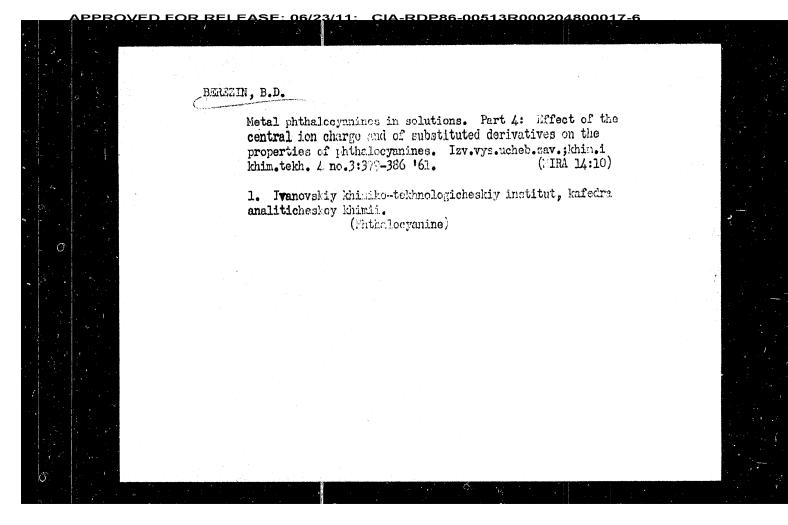
solution

FERTODICAL: Zhurnal neorganicheskoy khimii, v. 6. no. 12, 1961, 2672-2679

TEXT: The author studied less stable phthalocyanines of metals by the solubility method, and stable ones by means of isotopic exchange. The decomposition of less stable Pc follows the reaction $\text{MPC}_{\text{sol}}^{+2} + 2\text{H}_{3}^{0} + 2\text{H}_{4}^{2} + 4\text{H}_{2}^{2} + 4\text{H$

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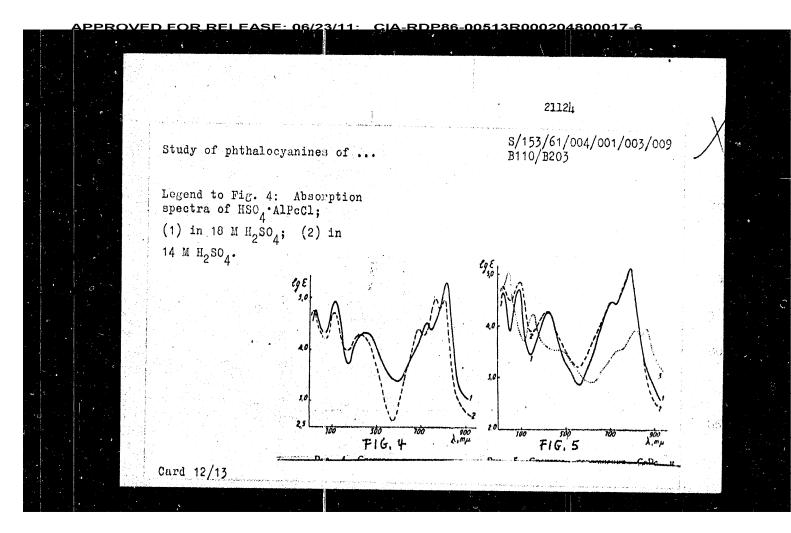
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Legend to Fig. 5: Absorption spectra CoPc and CuPccl 15;

(1) CoPc in 18 M H₂SO₄;

(2) CoPc in 15 M H₂SO₄;

(3) CuPcCl 15 in 18 M H₂SO₄.



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Study of phthalocyanines of ...

Eagend to Fig. 1: Abscription epectra of CuPc and H₂Pu;

(1) CuPc in 18 M H₂SO₄;
(2) CuPc in 15 M H₂SO₄;
(3) CuPc in α-C₁₀H₇Cl;
(4) H₂Pc in α-C₁₀H₇Cl.

Card 11/13

21124 S/153/61/004/001/003/009 B110/B203 Study of phthalocyanines of ... Legend to Table 2: Position а Элект-ронные of main electron transitions in solutions of MePc in α -C₁₀H₇Cl; (a) electron 11 Ш переходы **b** Фтало- $\lambda_{max+m\mu}$ цианин transitions, (b) phthalecyanine. H₉Pc CuPc NIPc 700 680 676 672 680 691 665605 614 602 604 604 622 CoPc ZnPc 345 CI · AIPc Card 10/13

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Study of phthalocyanines of ...

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 $\texttt{CuPcCl}_{15}\textbf{H}^{+} \texttt{ red-brown.} \quad \texttt{Desolvatation of MePcH}^{+} \texttt{ effects a slight change of }$ $oldsymbol{\lambda}_{ ext{max}}$ as well as of the absorption intensities by interaction of the proton with nitrogen, and, thus, a stronger polarization effect on the π-cloud of the macrocycle. This explains the weak bathochromic shift with increasing H2SO4 concentration. The latter has, however, no influence on the position of absorption maxima, which excludes the addition of a second proton to the $MePcH^+$, and proves their existence as monovalent bases at any acid concentration. In the aluminum complex (Fig. 4), a dissociation change according to the scheme: $[HSO_4 \cdot Al \cdot Po < Cl_H]^+ \longrightarrow HSO_4 + [Al \cdot Po < Cl_H]^{2+}$ is likely to take place. K. B. Yatsimirskiy is mentioned. There are 5 figures, 2 tables, and 18 references: 8 Soviet bloc and 10 non-Soviet bloc. The two references to English-languago publications read as follows: R. Williams: Chem. Revs., 56, 299 (1956); W. Caughey, A. Corwin: J. Amer. Chem. Soc. 77, 1509 (1955).

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Study of phthalocyanines of ...

values for the bonding strength metal - addendum, and for the position and intensity of maxima, are likely to give similar sequences. Table 1 shows for $\Lambda_{\rm max}$ of the MePcH the order: $\rm H_2Pc > ^{\rm t}AlPcCl > CuPc > \rm CoPc(ZnPc) > NiPc$, which agrees well with values of the mesoporphyrine complexes: $\rm Zn^{2+}$ (570 mm) $> \rm Cu^{2+}$ (561 mm) $> \rm Co^{2+}$ (552 mm) $> \rm Ni^{2+}$ (550 mm). Also here, the Ni complex for which maximum stability is assumed shows the minimum value. The irregularity of ZnPcH is explained as follows: The order of the MePcH with respect to the π -electron density does not agree with the order of the MePcH with respect to $\lambda_{\rm max}$, since the same π -electron density of the macrocycle may result from different fractions of σ - and π -bonds, which, in turn, have different effects on the λ shift. Also the transition intensity log ξ is not simply dependent on electron density. Polarization of bonds of benzene nuclei and the electron density. Polarization of bonds of benzene nuclei and the macrocycle in CuPcCl (Fig. 5) effects alleviation of transitions in the macrocycle as well as between the conjugate systems macrocycle benzene nuclei; maxima are bathochromically shifted: CuPcCl 15 is green, Card 5/13

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Study of phthalocyanines of ...

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symmetric molecule whose π -electron system is stabilized by double $p_{\pi}^{-d}_{\pi}$ bonds of the central ion with the addendum. New maxima are not formed, the metal ion is not chromophorous, since the weak transitions on the d-electron shells do not appear in the spectrum. Thus, the nature of transitions and the ionic structure are equal, in principle, for protonized H_2 Pc and MePcH⁺. The spectral shift (color change: deep green \rightarrow yellowish brown) observed in protonized H_2 Pc after standing for 48 hr is being studied now. On introduction of the covalent metal ion, 4 σ bonds of the central ion are formed at the expense of the completing of ion levels $3d4s4p^2$ (Co^{2+} , Ni^{2+} , Cu^{2+}); $4d4s4p^2$ (Zn^{2+}); $3d3s3p^2$, or higher levels (Al), by electrons of unbound electron pairs of intracyclic N atoms. Then, two simple oscillating π -bonds are formed with the π -cloud of the addendum by the d_{zx} and d_{zy} electron orbits of the metal ions unless they have been claimed by σ -bonds. The author had already established an increase of the π -electron density in the order: $CuPcCl_{15}$

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Study of phthalocyanines of ...

the intracyclic N atoms have lost the noncovalent electron pairs by complex formation. A $\pi_C \to \pi_N$ (3), and a $\pi_N \to \pi_C$ (4) transition are likely to occur in MePc. (3) corresponds to minimum exciting energy and produces the longwave absorption band. In (4), part of the $\pi\text{-cloud}$ passes from the more electronegative N to C, which produces the less intensive, longwave band. The $\pi_C \to \pi_C^{**}$ electron transition from the

conjugate benzene system to the macrocycle system may produce the absorption band in the adjacent ultraviolet range. Due to the high autonomy of the two systems, nearly 80 koal are required to this end. Besides, a transition from the macrocycle to the benzene ring, and a $\pi_{C} \rightarrow \pi_{C}^{*}$

transition in the substituted benzene ring are also possible. Protonization does not interfere with conjugation in the macrocycle, but it strongly polarizes the π -electron cloud by positive charge. Thus, this cloud becomes very mobile, and may be even excited by low-energy photons. Colors are deepened, and maxima are bathochromically shifted according to the color theory. On introduction of metals in the Po molecule, the intensity of maxima drops, probably due to the formation of a perfectly

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Study of phthalocyanines of ...

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of absorption bands. Co, Ni, Cu, and Zn salts dissolved in 8-10 M H2SO4 are assumed to have monovalent, basic character: (MePc) dis + H2SO4 - MePcH+ + HSO4. Thus, metal salts protonized in H2SO4 solution can be studied in the spectrum for rules basing on the exchange of metals and substituents in the complex, on charges in the central ion, etc. The proton bound in H2SO4 solution to the conjugate ring system does not change the character of electron transitions but their probability (bathochromi: shift = 80-120 m μ , drop in excitation energy: infrared range 5-6 kcal, ultraviolet range = 16 kcal). This, and similar conditions for other MePo (Tables 1 and 2), is explained as follows: $n \to \pi^*$ (1) and $\pi \to \pi^*$ (2) transitions are possible in the Fc molecule. In (1), an unbound electron passes from the noncovalent pair of N atoms to the shell of the π -electron cloud of the macrocycle. In (2), a π -electron within the conjugate system passes from the electron shell of one atom to that of another atom. In Pc molecules, probably only (2) exists, since electron spectra of phthalocyanines and porphyrines are very similar. In metal pheophytinates, (2) is no longer possible since

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AUTHOR:

Berezin, B. D.

TITLE:

Study of pathalocyanines of metals in solutions.

III. Absorption spectra of phthalocyanines in sulfuric

acid solutions

PERIODICAL:

Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, v. 4, no. 1, 1961, 45-52

TEXT: To study photosynthetic and biological reaction chemisms in the living organism, the absorption spectra of porphyrine derivatives are very important for their identification. In the present study, the author uses strong sulfuric acid solutions of stable metal phthalocyanines: chemically pure Cu, Zn, Go, Ni salts, HEO4* AlPoCl (according to Linstead),

CuPcCl 15, and free $\rm H_2Pc$. Sulfuric acid solutions with strong $\rm H_2SO_4$ of known titer were prepared. The absorption spectra in the ultraviolet, visible, and adjacent infrared spectrum ranges were taken at 22-24°C by an $\rm C\bar{\Phi}$ -4 (SF-4) spectrophotometer. Table 1 gives maxima and intensities

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BEREZIN, B.D.; POGODINA, L.G. Phloroglucinol an an indicator in mercurimetry. Zav.lab. 26 no.12: 1347-1351 '60. (MIRA 13:12) (MIRA 13:12) 1. Ivanovskiy khimiko-tekhnologicheskiy institut.
(Phloroglucinol) (Mercurimetry (Mercurimetry)

SOV/153-2-2-4/31 Investigation of the Metallic Phthalocyanines in Solutions. II. Acidic-alkaline Interaction of the Phthalocyanines of Some Metals in Sulphuric-acid

X-ray structural data as well as with the chemical and physico-chemical properties of the phthalocyanines. K. B. Yatsimirskiy read the manuscript. V. F. Borodkin supplied the phthalocyanine preparations. There are 2 figures, 2 tables, and 9 references, 3 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut; Kafedra ana-

liticheskoy khimii

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SUBMITTED: January 9, 1958

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Investigation of the Metallic Phthalocyanines in Solutions. II. Acidic-al-kaline Interaction of the Phthalocyanines of Some Metals in Sulphuric-acid Solutions

4 metals mentioned before as well as for HoPc were computed (1). Tables 1 and 2 show the indices of these constants (computed by formula 4). The pKMPc-values keep a good constancy over a considerable range of acidity. For a perfect confirmation of his assumptions and computations, the author determined the solubility of CuPe and CoIc in 16.70 m $\rm{H}_{2}SO_{4}$ and of ZnPc in 17.25 m H2SO4. It is in good agreement with the values computed by equation (4). So it can be assumed that equation (4) only applies to ${\rm H_2SO_4}$ up to 100% concentrations. This equation is useless for oleum since stronger acids, such as H₃SO₄⁺ et al (Ref 7), are present in it. From the experimental results of the present paper, one can make theoretical conclusions which are connected with the dependence of the MPc-solubility on the nature of the metal. On the basis of his investigation of the phthalocyanine properties, the author suggests modified structure formulas of the free phthalocyanine and its covalent complex salts (Fig 2). They are in good agreement with the

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Investigation of the Metallic Phthalocyanines in Solutions. II. Acidic-al-kaline Interaction of the Phthalocyanines of Some Metals in Sulphuric-acid

they lead to formulas which are useful for the practical computation of the dissolution of phthalocyanine dyes in H2SO4 (and other concentrated acids) in their industrial purification. The derivation of the mentioned formulas is based on the fact that 4 peripheral, so-called extracyclic, nitrogen atoms are present in the molecule. They carry free electron pairs which give the phthalocyanines the properties of very weak bases. In the opinion of the author, this is due to the participation of free electron pairs of the extracyclic nitrogen atoms in the composition of a metalline molecule (Ref 2). The author assumes that the metallic phthalocyanines can only absorb one proton in a noticeable degree. This proton considerably weakens the basic properties of the MPcH as it intensely deforms the π -electron cloud of the conjugate large ring in the direction of the absorbed proton. This assumption was well confirmed by the experimental results of the present paper. From the data on the solubility, the equilibrium constants KMPc for the reaction (II) for the phthalocyanines of the

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