faster than the other for a wide range of concentrations.[12]

It should be emphasized that analytical determinations of copolymer composition as a function of conversion will yield information about ρ and σ only and not of any other parameters involved. To get the absolute values of the specific reaction rate constants it would be necessary to know something about the radical concentrations, which information is not readily available. A direct measurement of ρ and σ for the system methyl methacrylate and styrene has been carried out by Mayo and Lewis.[4] Their results indicate that $\rho = \sigma = 0.5$. This means that methyl methacrylate and styrene constitute a pair that is qualitatively similar to that illustrated by Fig. 3.

Numerous examples are available for systems in which σ (or ρ) is equal to zero. The early work of Wagner–Jauregg[13] on maleic anhydride and ethylene derivatives provides such examples. Maleic anhydride does not polymerize with itself but readily polymerizes with substances like styrene with a marked tendency to form a 1:1 polymer. It appears quite likely that maleic anhydride and styrene belong to a system similar to that of Fig. 6. The azeotrope will have a composition very nearly 1:1 but not exactly. If one starts with an excess of styrene, the first polymer will be close to the azeotrope, but the last polymer formed will be pure polystyrene. It would be incorrect to suppose, however, that no polymer chains could have intermediate compositions.

Other systems whose behaviors can be explained by setting σ (or ρ) equal to zero include ethylene derivatives in conjunction with sulfur dioxide[11] or with maleic imides.[14] In most cases sulfur dioxide appears to form approximately 1:1 azeotropes with the ethylene derivatives indicating that ρ is small compared to unity while $\sigma = 0$. On the other hand, vinyl chloride and sulfur dioxide may well form a 2:1 azeotrope,[11] suggesting that $\rho = 0.5$ while $\sigma = 0$.

Unless both ρ and σ are equal to zero one does not form exactly the so-called heteropolymers[13] which have regular alternations of monomer units. Many apparent heteropolymers are probably azeotropes for which $\rho = \sigma \neq 0$ or are systems for which $\sigma = 0$ and $0 < \rho \ll 1$.

Summary

Using the concepts of Norrish and Brookman,[8] a general theory of copolymerization is developed which involves relative polymerization velocities as functions of the monomer composition. The treatment is developed in analogy to vapor pressures of binary systems. The ideal systems[1] (corresponding to "Raoult's Law" type of behavior) are suggested as starting concepts from which deviations might be observed. Non-ideal copolymerization systems can sometimes lead to "azeotropic copolymers." The nature of such "azeotropes" together with their intramolecular distributions are considered. The behavior of certain polymerization systems, particularly those leading to so-called heteropolymers are accounted for by the theory.

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(12) Staudinger and Schneiders, *Ann.*, **541**, 151 (1939).

(13) Wagner–Jauregg, *Ber.*, **63**, 3213 (1930).

(14) Arnold, Brubaker and Dorough, U. S. Patent 2,301,356 (1942).

URBANA, ILLINOIS RECEIVED JULY 22, 1944

[CONTRIBUTION FROM THE APPLIED SCIENCE RESEARCH LABORATORY OF THE UNIVERSITY OF CINCINNATI AND THE CINCINNATI MILLING MACHINE COMPANY]

Action of *n*-Primary Alcohols as Metal Cutting Fluids—Alternating Properties with Chain Length

BY MILTON C. SHAW[1]

It is customary to introduce some form of cutting fluid at the chip–tool interface when metal is removed from a work-piece by means of a cutting tool. The purposes of the cutting fluid are to facilitate the removal of metal and to produce a smooth surface finish. A large variety of fluids have been used in the metal working industry in the past but little attempt has been made to correlate the efficiency of a cutting fluid with the physical and chemical properties of the liquid–metal combination. As part of a broad study of the mechanism of cutting fluid action, the metal cutting efficiency of pure *n*-primary alcohols has been investigated using a carefully controlled cutting technique.

All the normal, primary, monohydric alcohols from methanol to dodecanol were used in this investigation. The absolute methanol and absolute ethanol were used in their commercial form. The other alcohols were fractionated before using in a distillation apparatus with an efficiency of about nine theoretical plates. Pure distilled water was included as the first member of the series.

The manner in which the tests were made is shown diagrammatically in Fig. 1. A chip was cut from an aluminum work block using a high speed steel finishing-type planer tool having a

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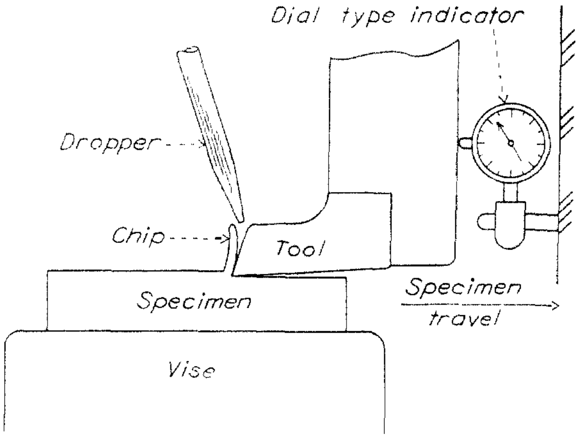

Fig. 1.—Metal cutting apparatus.

top rake angle of 15° and a clearance angle of 3°. All tests were made at the very low cutting speed of 5.50 inches per minute and the depth of metal removed was 0.005 inch. The space between the tool and the work-piece was kept filled with the liquid being tested by means of a dropper.

The force necessary to remove a chip from the aluminum work block was measured by a previously calibrated dial type indicator showing the deflection of the tool holder in units of 0.0001 inch. Each 0.0001 inch division of the indicator was equivalent to a force of 5.65 pounds and readings were estimated to the nearest 0.00001 inch. From a large number of successive cuts, it was found that individual determinations varied from the average by a maximum of 0.00002 inch or 1.13 pounds. No attempt was made to separate the precision of the measuring device from the reproducibility of the cutting process and the foregoing values are for the combined deviations.

At the beginning of a cut, the force rose quickly to a steady value which remained constant during the remainder of the excursion within the least detectable variation on the dial indicator (0.00001 inch or 0.57 pound). The steady value of cutting force was reached after the tool had traversed about 0.25 inch of the three inch long specimen. It is important that the keenness of the cutting tool remain constant throughout the entire series of tests and a check on this was made between each pair of alcohols by making cuts using carbon tetrachloride. These check values were the same within the experimental accuracy cited above and thus attest the constancy of the cutting edge.

All of the tests were made on the same specimen of annealed commercially pure 2S aluminum which measured 3 by 3 by 0.25 inches, thus ensuring a material of constant initial hardness and structure. Since the force required to remove a chip depends upon the amount of work hardening of the surface metal produced in making the previous cuts, it was found necessary to discard the first two or three determinations until the surface reached a steady condition. The following sequence is cited to illustrate this point.

Cutting force using carbon tetrachloride	52.0 lb.
First cut using ethanol	76.5 lb.
Second cut using ethanol	74.0 lb.
Third cut using ethanol	73.0 lb.
Fourth cut using ethanol	73.5 lb.
Fifth cut using ethanol	73.0 lb.

In this case, the readings starting from the third cut with ethanol were averaged to obtain the characteristic value for this fluid.

It was found that when pure, normal, primary, monohydric alcohols are used in metal cutting, the force necessary to remove a standard size chip from an aluminum work block under uniform conditions alternates with the use of successive members of the alcohol series. Figure 2 is obtained by plotting the cutting force against the number of carbon atoms in the alcohol chain. The alcohols having an odd number of carbon atoms in their chain are seen to be more efficient in this particular metal cutting operation than the compounds having an even number of carbon atoms.

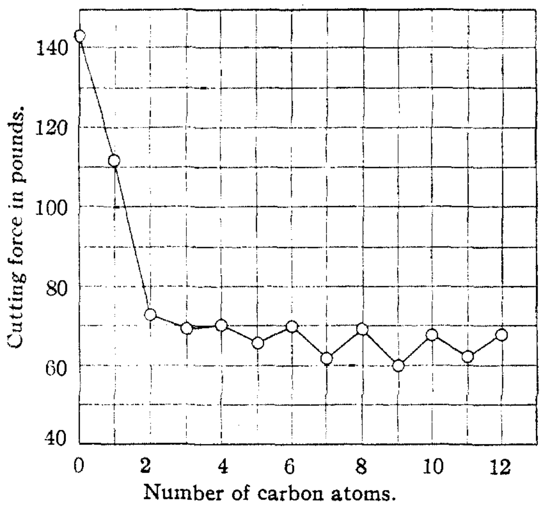

Fig. 2.—Cutting force with normal aliphatic alcohols as cutting fluids.

While there are many references in the literature to the periodic variation of such properties as melting point, viscosity, heat and entropy of crystallization, molecular volume and other physical properties of successive members of homologous series,[2] little has been reported concerning similar periodic alternations of chemical properties.

Challenor and Thorpe[3] have mentioned that they observed a difference in the ease with which even and odd members of the dibasic acid series are oxidized. A borderline case which may be considered either physical or chemical in nature,

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[2] H. Gilman and Others, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, Vol. 2, p. 1720.

[3] W. A. P. Challenor and J. F. Thorpe, *J. Chem. Soc.*, **123**, 2480 (1923).

is reported by Biltz and Balz[4] who measured the dissociation pressure of various ammonia salts and found that these pressures alternated as the series was ascended. An alternation in the yield of Grignard reagents with alkyl iodide chain length has been reported by Gilman and McCracken.[5]

In general, metal cutting is accompanied by a high surface temperature, high pressure between the moving surfaces and the production of a considerable area of clean, highly reactive surface. Fluid film formation, common to ordinary types of lubrication, plays no part in metal cutting. The mechanism of cutting fluid action is obviously a problem in the extreme boundary region of lubrication. While much evidence has accumulated to uphold the role of adsorbed surface films in reducing the frictional resistance of sliding surfaces under relatively mild boundary lubrication conditions,[6,7,8] another mechanism is believed to obtain in the extreme boundary region of lubrication.[9] In the extreme boundary region, an effective fluid is believed to enter into a surface chemical reaction with the metal being cut to produce a low shear strength metal salt. The frictional resistance is considerably lowered if metal-to-metal contact is reduced by the formation of such a metallic compound between the sliding surfaces. Thus, it is believed that the alternating properties here displayed by the alcohol–aluminum combination is a chemical phenomenon.

Acknowledgment.—The writer wishes to acknowledge the coöperation of the staff members of the Applied Science Research Laboratory of the University of Cincinnati and of the Research Laboratory of the Cincinnati Milling Machine Company.

Summary

An alternation in the cutting force required to remove a chip from an aluminum block at very low cutting speed is noted when successive normal, primary, monohydric alcohols are used as cutting fluids. Alcohols having an odd number of carbon atoms require lower cutting forces than the compounds having an even number of carbon atoms.

[4] W. Biltz and G. Balz, *Z. anorg. allgem. Chem.*, **170**, 342 (1928).

[5] H. Gilman and R. McCracken, THIS JOURNAL, **45**, 2462 (1923).

[6] Sir W. B. Hardy, "Collected Works," Camb. Univ. Press, 1936.

[7] L. T. Andrews, *Trans. Faraday Soc.*, **32**, 607 (1936).

[8] N. K. Adam, "General Discussion on Lubrication and Lubricants." Institution of Mech. Engrs. (Amer. Ed.), 1937, Vol. 2, p. 197.

[9] M. C. Shaw, *Metal Progress*, **42**, 85 (1942).

CLEVELAND, OHIO RECEIVED JULY 12, 1944

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF UNIVERSAL OIL PRODUCTS COMPANY]

Effects of Temperature, Contact Time, and Water Vapor on the Olefin–Aromatic Ratio in the Dehydrogenation of *n*-Heptane with Chromia–Alumina

BY WILLIAM J. MATTOX

Some of the more recent publications[1–8] on the aromatization of aliphatic hydrocarbons have contained discussions relative to the formation of olefins and their role in the mechanism of the cyclization reaction. In most instances with chromia-containing catalyst where the corresponding olefin yields have been reported, the olefin–aromatic ratio in the reaction products decreases with increased contact time. With the exception of comparatively short contact times, the ratio is usually less than 1. For example, the data of Pitkethly and Steiner,[3] obtained at 475°, show olefin–aromatic ratios greater than 1 only at contact times of less than about nine seconds.

In connection with work reported previously,[9] and to some extent as observed in the published work of others,[3,10] variations in certain conditions under which the aromatization reaction may be carried out were observed to influence the proportion of olefins in the recovered products. Taylor and Turkevich[11] observed that water vapor, which is strongly absorbed by chromium oxide gel, is a marked poison for the aromatization reaction. Salley, Fehrer and Taylor,[12] in studying the addition of water vapor in 0–3 mole per cent., state that the retardation effects involve a decrease of toluene, but not of olefins. The highest olefin–aromatic ratio calculated from the data reported by these investigators, however, is 0.43.

The present paper constitutes a summary of a more extensive investigation of some of the effects of temperature, contact time or space velocity, and water vapor at atmospheric pressure. The

[1] Goldwasser and Taylor, THIS JOURNAL, **61**, 1766 (1939).

[2] Hoog, Verheus and Zuiderweg, *Trans. Faraday Soc.*, **35**, 993 (1939).

[3] Pitkethly and Steiner, *ibid.*, **35**, 979 (1939).

[4] Kazansky, Sergienko and Zelinsky, *Compt. rend., acad. sci. U. R. S. S.*, **27**, 664 (1940); Universal Oil Products Co., Survey of Foreign Petroleum Lit. No. 291, Feb. 7, 1941.

[5] Oblad, Marschner and Heard, THIS JOURNAL, **62**, 2066 (1940).

[6] Turkevich, Fehrer and Taylor, *ibid.*, **63**, 1129 (1941).

[7] Fehrer and Taylor, *ibid.*, **63**, 1385 (1941).

[8] Sergienko, *Inst. of Org. Chem., Acad. Sci. U. R. S. S.*, 177–190 (1941); Universal Oil Products Co., Survey of Foreign Petroleum Lit. No. 370, Jan. 22, 1943.

[9] Grosse, Morrell and Mattox, *Ind. Eng. Chem.*, **32**, 528 (1940); reprinted in Universal Oil Products Co. Booklet No. 241.

[10] Taylor and Fehrer, THIS JOURNAL, **63**, 1387 (1941).

[11] Taylor and Turkevich, *Trans. Faraday Soc.*, **35**, 921 (1939).

[12] Salley, Fehrer and Taylor, THIS JOURNAL, **63**, 1131 (1941).