TABLE I

PHYSICAL CONSTANTS, APPARENT IONIZATION CONSTANTS (25°) AND DIPHENYLDIAZOMETHANE REACTION RATE CONSTANTS (30°) OF 4-SUBSTITUTED 2,6-DIMETHYLBENZOIC ACIDS

Substituent	M.p., °C.	Half-point[a]	$K \times 10^6$ [b]	Concn. of acid,[c] moles/l.	Half-life,[c] min.	Av. k_2 l./mole min.
n-C_3H_7O–	93.0– 94.0	5.48	3.3	0.0423	6.92, 6.90	2.37
CH_3–	154.5–155.2	5.38	4.2	.0605	10.22, 10.25	2.80
CH_3CONH–	220 –222	5.21	6.2	.0389	5.33, 5.33	3.35
H–	115.5–116.2	5.18	6.6	.0231	8.25, 8.25	3.64
Br–	194.8–195.3	4.78	16.6	.0273	4.56, 4.58	5.53
H_2NCO–	246 –248	4.65	22.4	.0119	9.58, 9.58	6.09
CH_3O_2C–	191.0–192.0	4.56	27.5	.0126	7.92, 7.92	6.94

[a] Reading on pH scale of pH meter calibrated for aqueous buffer solutions at half-neutralization point using glass and saturated calomel electrodes without correction for liquid junction potentials in 50% water–50% ethanol (by volume) solutions. [b] Calculated assuming unit activities and readings of pH meter scale equal to logarithm of reciprocal of hydrogen ion concentrations.

linear free-energy relationship of the usual sort.[4] Plots of pK_A and log k_2 against the available Hammett σ-constants[4] are given in Figs. 1 and 2. It was assumed that the σ-constants of the p-n-propoxy and p-carbomethoxy groups are equal to those for p-methoxy[4,5] and p-carboethoxy[6] groups, respectively.

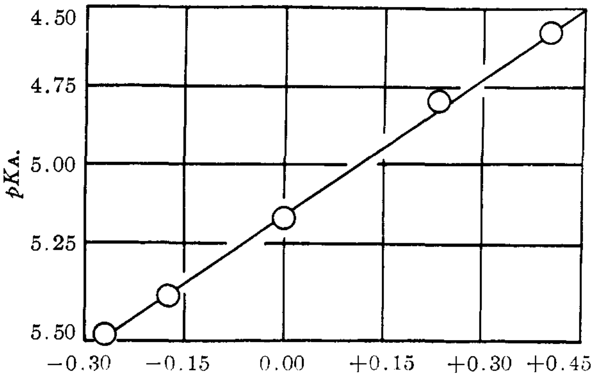

Fig. 1.—pK_A and σ for 4-substituted 2,6-dimethylbenzoic acids, points given for n-propoxy, methyl, hydrogen, bromo and carbomethoxy as 4-substituents.

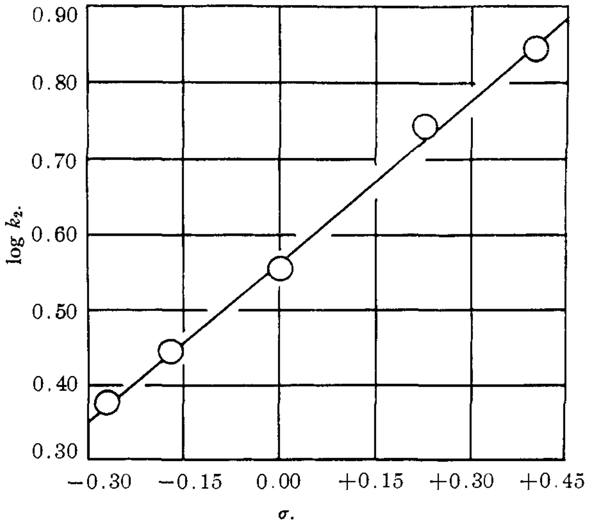

Fig. 2.—Log k_2 and σ for 4-substituted 2,6-dimethylbenzoic acids; points for substituents as in Fig. 1.

The plots of Figs. 1 and 2 show no pronounced upward trend with the electron-donating n-propoxy group as would be expected if electrical coupling between carboxyl group and substituent group (as expressed by II) were important in 4-substituted benzoic acids and sterically inhibitable by methyl groups ortho to the carboxyl. It is possible that such effects might be important in benzoic acids with more strongly electron-donating p-substituents.

II

Acknowledgment.—We are indebted to Dr. M. S. Newman for information in advance of publication about his own research on this problem,[7] and to Dr. Newman and Dr. R. V. Heinzelman of the Upjohn Company for generous samples of the acids used in this work.

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(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chaps. III, VII and IX.

(5) The assumption looks quite reasonable since p-methoxy and p-ethoxy have almost identical σ-constants.[4]

(6) J. D. Roberts and W. T. Moreland, Jr., THIS JOURNAL, **75**, 2267 (1953).

(7) H. L. Goering, T. Rubin and M. S. Newman, *ibid.*, **76**, 787 (1954).

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A Method for Growing Barium Titanate Single Crystals

BY J. P. REMEIKA

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New types of storage elements for digital computers and telephone switching systems are under investigation which have as a basic requirement a rectangular hysteresis loop characteristic.[1] This property may be obtained in ferromagnetic as well as in ferroelectric materials. The most promising of the ferroelectrics is barium titanate which may be used either as a single crystal or as a ceramic.[2] Our work on ferroelectric storage elements has indicated that the hysteresis loops obtained from

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(1) J. R. Anderson, *Elec. Eng.*, **71**, No. 10, 916 (1952).

(2) A. Von Hippel, *Rev. Modern Phys.*, **22**, 221 (1950).

barium titanate single crystals are more rectangular than those from ceramics. Of importance for telephone switching applications also is the fact that, at least in specially prepared single crystals, the coercive force, *i.e.*, the field required to reverse the polarization, is much lower than in ceramics.

Barium titanate crystals have been grown by several different methods but we have not observed in any of them the desired rectangular hysteresis loops at sufficiently low fields. This includes crystals grown from $BaCl_2$ solutions by the method of Blattner, Matthias, Merz and Scherrer,[3] by the flame fusion method and from the pure melt by the Stockbarger process.

We have developed a method of preparing barium titanate crystals which yields large, clear single crystals having the desired ferroelectric characteristics. Furthermore these crystals are obtained in the form of thin plates which lend themselves readily to storage device applications.

A typical procedure by which it has been possible to grow good single crystals of barium titanate is to start with a mixture containing approximately 30% of barium titanate (C.P.), 0.2% of ferric oxide (Reagent) and the balance of potassium fluoride (C.P. Anhydrous). The barium titanate and ferric oxide are placed in a platinum crucible (standard low form) and then covered with the potassium fluoride. The crucible containing this charge is covered with a platinum lid and placed directly into a furnace which is at a temperature between 1150 and 1200°. The furnace is held at this temperature for eight hours and then cooled at a slow constant rate until a temperature of 850 to 900° is reached. The still liquid flux is poured off at this point and the crystals are annealed by slowly cooling down to room temperature. This particular procedure is one adapted to our equipment and may of course be varied. The important considerations are (1) to get a considerable quantity of barium titanate in solution, (2) to allow crystallization to take place slowly enough to minimize unwanted nucleation, but fast enough to preserve the plate habit, and (3) to anneal the crystals by slow cooling in an unstrained condition.

Two different habits of crystal growth are observed in these experiments. A mass of chunky crystals is usually found on the bottom of the crucible. Growing out of this layer are numbers of thin plates, always in pairs, which for lack of a better name are called butterfly wings. These extend upwards into the melt. The crystal plates may be separated from the flux by soaking the crucibles in hot water which dissolves the fluoride rapidly. The thin plates produced in this way have been found to be more perfect and approximate more nearly to "single domain" crystals than any others which have come to our attention. By this is meant that thin, large area crystals are obtained which are relatively free from so called 90° walls and in which the polar direction (*c*-axis) is usually perpendicular to the major crystal faces. This is important for obtaining the desired rectangular hysteresis loops and low coercive force. Some of the characteristics of these barium titanate single crystals have been described by Merz.[4]

Many of the early barium titanate crystals were found to be dark colored and to have too high a conductivity for storage circuit applications. This might be traceable either to impurities or to a loss of oxygen during the crystal growing process. We have found that crystals with much lower dielectric loss are obtained if a small amount of Fe_2O_3 is added to the melt from which they are grown. Measurements were made by Mr. F. J. Morin of these laboratories of the sign of the thermoelectric effect in barium titanate crystals containing various amounts of added iron. It was observed that crystals grown in potassium fluoride without added Fe_2O_3 were *n*-type semiconductors at elevated temperatures. This may be the result of the loss of oxygen resulting in donor ions being produced. The addition of Fe_2O_3 supplies acceptor ions and if the number of these is just such as to compensate for the donors the crystals become intrinsic semiconductors. A minimum of conductivity and a change of sign of the thermoelectric effect are observed at about 0.2 atomic percentage of added iron. The amount of iron required for this compensation depends upon the conditions of growing the crystal, *i.e.*, upon the presence of other impurities and the amount of loss of oxygen. The latter in turn depends upon the temperature of crystallization and the time that the melt was held at high temperatures. It is observed also that the iron lowers the Curie temperature very markedly. Crystals containing 0.2% iron have a Curie temperature of about 105 to 110° while those containing 2.5 atomic percentage of added iron are cubic at room temperature. X-Ray studies by Mrs. E. A. Wood have shown that the *c*/*a* ratio decreases with added iron.

This procedure for growing barium titanate crystals has been useful for producing crystals for experimental purposes. The choice of potassium fluoride as a solvent is a good one from the standpoint of solubility of barium titanate. However, it should be pointed out that it reacts readily with the furnace refractories so that their life is short. The usual precautions in handling fluorides should be observed and such work should, of course, be done only in a well ventilated space.

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[3] Blattner, Matthias, Merz and Scherrer, *Helv. Chim. Acta*, **30**, 225 (1947); *Experientia*, **3**, 4 (1947).

[4] W. J. Merz, *Phys. Rev.*, **91**, 513 (1953).

Low Concentration Chemistry. VII. Investigations on the Role of Adsorption in Radiocolloid Formation

BY GEORGE K. SCHWEITZER AND W. MORRISON JACKSON

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Radiocolloid formation has been attributed by some investigators to an adsorption of cations in very low concentrations upon negatively charged impurities in basic solutions, thus simulating true colloids.[1] If this adsorption of ions upon impurities is a factor of primary importance in radiocolloid formation, then it should be possible to assume that anions in low concentrations would behave accordingly and be adsorbed upon positively charged impurities in acid solutions, thus also simulating colloids. Also, if adsorption is an important factor cations which do not form insoluble hydroxides should show radiocolloidal behavior as well as those which do. The purpose of these experiments was to test the assumption that the primary factor in

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[1] G. K. Schweitzer and M. Jackson, *J. Chem. Education*, **29**, 513 (1952).