Smears of Titanium Metal

A REMARKABLE phenomenon is shown by metallic titanium when rubbed against many hard surfaces. If a piece of the metal with a rounded end, of radius of curvature about 1 mm., is pressed firmly on to a hard surface and drawn across it, the metal is left behind in the form of a silvery smear. Smears are obtained with greater difficulty on some substances than on others, but only one crystalline material has been found on which no smear is produced (see accompanying table). The titanium metal may be removed by treatment with hot concentrated hydrochloric or sulphuric acids for about half an hour, or by treatment with cold commercial hydrofluoric acid for a few seconds. Some surfaces which were originally smooth and shiny are seen to have lost their polish after the titanium has been dissolved away. In this way, for example, it is possible to remove the polished surface of glass by rubbing with titanium and then dissolving the metallic smear in hydrochloric acid. The table gives a summary of the results obtained on a number of crystalline materials and on glass.

On Moh's scale the hardness of titanium is less than 5, since it is scratched by apatite but not by fluorspar. It will be seen that in the first place we have the result that a material of hardness 5 can destroy the surface of a crystal of hardness 8, namely, topaz¹. Among the oxides the surface smoothness is affected only with difficulty or not at all, whereas all the silicates except beryl are readily attacked.

Chemical reaction brought about by rubbing two materials together is well known, and these effects may be due to some chemical reaction of the titanium with the materials on which it is rubbed. The readiness with which silicates react suggests that the titanium may enter into the lattice.

The practical applications of the smears may be (a) to coat materials with a metallic layer, (b) to etch glass without hydrofluoric acid, and (c) to form high resistances of the order of 10^{11} ohms; lines drawn on glass form such resistances, and although not stable against all changes of atmospheric conditions, they are sufficiently stable to be useful.

This investigation arose from a suggestion of Mr. J. B. Nelson and was made possible by a gift of a

Name	Substance		Smear produced		Polish on surface removed		
	Chemical formula	Hard- ness (Moh's scale)	Read- ily	Not at all	Com- pletely	Par- tially	Not at all
Diamond	C	10	×				×
Corundum Hæmatite	Al ₂ O ₃	9	×				×
(specular) Hæmatite (kidney	Fe ₂ O ₃	5.5-6.5	×			×	
ore)			1	X	i i		×
Magnetite	Fe ₃ O ₄	5.5-6.5	××			×	
Rutile Chryso-	TiO ₂	6	×			×	
beryl	BcO.Al ₂ O ₃	8.5	×				×
Spinel	(Mg, Fe)O, Al ₂ O ₃	8	×				×
Quartz	SiO.	8 7 8	* * * * *		×		
Topaz	(Al.F) SiO	8	×		×××		1
Diopside	CaMg(SiO ₂) ₂	5-6	×	i	×		
Beryl	Be 8Al Si O18	8	×				X
Albite Axinite	NaAlSi ₃ O ₈ HCa ₃ BAl ₂	6	×		×		
	(SiO ₄) ₄	7	×		×		
Epidote	HCa ₂ (Al,Fe) ₃ Si ₃ O ₁₃	6-7	l ×		×		
Garnet	Ca ₃ Al ₂ (SiO ₄) ₃	7	×			×	
Tourm-	(0104/8		1				
aline	1	7	×		×		
Glass		75	××		××		

piece of titanium from Mr. H. F. Kay; we gratefully acknowledge this help. We are indebted to the Department of Mineralogy and Petrology for access to the mineral specimens on which the tests were made.

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¹ Bowden, F. P., Moore, A. J. W., and Tabor, D., *J. Appl. Physics*, 14, 80 (1948.)

Furansulphonamides

As a recent issue of *Chemical Abstracts* contains an account of the preparation of the sodium and barium salts of furan-2-sulphonic acid¹, by the direct sulphonation of furan, the following report on the indirect production, from pyromucic acid, of simple sulphonation derivatives of furan may be of interest.

The diamide of pyromucic-5-sulphonic acid was prepared, by the method of Hill and Palmer², and converted, with barium hydroxide, to furan-2-carboxylic acid-5-sulphonamide

$$C_4H_2O(CONH_2)SO_2NH_2 \longrightarrow C_4H_2O(COOH)SO_2NH_2.$$

Substituted sulphonamido acids were obtained from the dichloride of pyromucic-5-sulphonic acid, as indicated schematically below.

$$C_4H_2O(COCl)SO_2Cl \xrightarrow{CH_3OH} C_4H_2O(COOCH_3)SO_2Cl$$

$$\xrightarrow{R_1R_2\text{NH}} C_4\text{H}_2O(\text{COOCH}_3)\text{SO}_2\text{NR}_1R_2 \xrightarrow{\text{NaOH}}$$

 $C_4H_2O(COONa)SO_2NR_1R_2.$

The above acids were decarboxylated by the method of Gilman and Wright³.

$$C_4H_2O(COONa)SO_2NH_2(R_2)$$
 HgCl_

$$C_4H_2O(HgCl)SO_2NH_2(R_2) \xrightarrow{HCl} C_4H_3O.SO_2NH_2(R_2).$$

Furan-2-sulphonamide (m.p. 122-123.5°), furan-2sulphonyl methyl anilide (m.p. 95-98°) and furan-2-sulphonyl-diethylamine, a liquid, were thus prepared.

Furan-3-sulphonic acid and its derivatives were obtained as follows : Pyromucic acid was brominated to the 5-bromo acid, which was sulphonated and the carboxylic group replaced by bromine, as described by Hill and Palmer⁴. The barium 2-5 : dibromofuransulphonate thus obtained was treated with zinc and ammonium hydroxide, which replaced the bromine atoms by hydrogen, giving barium furan-3-sulphonate.

From this salt was prepared the *p*-toluidine salt (m.p. $172-173^{\circ}$), and the free acid, an oily liquid, which was reconverted into the barium salt, and the *p*-toluidine salt. The impure sodium salt was obtained, in the usual way, and converted into the sulphonic chloride, from which furan-3-sulphonamide (m.p. $106-108^{\circ}$) and furan-3-sulphonylmethylanilide (m.p. $95-97^{\circ}$) were prepared.

A detailed account of this investigation will appear shortly.

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¹ Terent'er, A. P., and Kazitoyra, L. A., *Chem. Abs.*, **41**, No. 7, 2033 (1947).

^a Amer. Chem. J., 10, 378 (1888).

³ J. Amer. Chem. Soc., 55, 3311 (1933).

4 Amer. Chem. J., 10, 413 (1888).