Eight small plates cut to 15×60 mm. are pickled simultaneously in 1.8 1. of $3.6 \sim 9.8\%$ H$_2$SO$_4$ solution at $10 \sim 90°$C. for various lengths of time ($0 \sim 90$ min.).

At first, it was ascertained that the volume of absorbed hydrogen by steel plates was not influenced by the existence of the rolled scale on them.

The volume of absorbed hydrogen increases for the initial 10 min. and decreases in longer pickling time. At 60°C., steel plates absorb the most hydrogen during 40 min. pickling with 6.8$\%$ H$_2$SO$_4$ solution.

The concentration of H$_2$SO$_4$ does not affect the degree of hydrogen absorption.

After pickling by 6.8$\%$ H$_2$SO$_4$ at 60°C. for 40 min., the pickled plates were kept at various temperatures. By holding at room temperature, the absorbed hydrogen hardly effuses, even in 20 days.

After holding the pickled steel plates in hot water of 60 and 90°C. for 90 hrs. these plates evolve respectively 30 and 40$\%$ of the initial volume of absorbed hydrogen by pickling.

In order to facilitate the detection of evolution of absorbed hydrogen, the iron sulphide powder was added to the pickling solution before pickling, as S$''$ ion promotes the absorption of hydrogen in steel. In this case, the volume of absorbed hydrogen reaches 55.6 cc./100grFe. in comparison with 4.6 cc./100 grFe. under the same condition without iron sulphide addition. And most of these absorbed hydrogen effuses at room temperature, and the remained hydrogen in steel reaches 5.32 cc./100grFe. after 15 days.

By holding in 60 and 90°C. hot water, the plates pickled with 6.8$\%$ H$_2$SO$_4$ solution containing S$''$ ion effuse 50 and 85$\%$ of the initial volume of absorbed hydrogen in 5 hours respectively.

"Rodine" or gelatine is added at various amounts to the pickling solution containing S$''$ ion in order to retard the hydrogen absorption. Of these inhibitors, "Rodine" shows the most favourable result, that is, addition of Rodine 0.09 gr./1. decreases the volume of absorbed hydrogen to 1/20 of that of absorbed hydrogen without this reagent.

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21. Synthesis of Some Fatty Acid Derivatives

Ryohei ODA, Kazuhiro TERAMURA and Hiroshi ITAGAKI

(Oda Laboratroy)

1. Reactions of Diethyl Decyl-malonate.

a) Synthesis of diethyl decyl-malonate. (I) $\text{C}_{10}\text{H}_{21}\text{CH}{<}^{\text{COOC}_2\text{H}_5}_{\text{COOC}_2\text{H}_5}$

The authors have prepared (I) by the action of diethyl oxalate upon ethyl laurate in the presence of sodium ethylate according to *J. Am. Chem. Soc*, **69**, 2354, (1947). Yield 87.3$\%$, b.p. 183–188°C/22mmHg.

b) Synthesis of decyl barbituric acid. $C_{10}H_{21}CH\overset{CONH}{\underset{CONH}{\diagup\diagdown}}CO$

Metallic sodium (6.9g.) was dissolved in 130g. of ethylalcohol; to this solution 30g. of (I) and 8.6g. of dried urea were added, and the mixture was heated on water bath. Immediately, white precipitate appeared; after 5 hours, the precipitate was filtered, dissolved in water, neutralized with HCl, filtered, and recrystallized from ethyl alcohol. Yield 25g. (90%), m.p. 194°C, N% 9.27 (Calcd. 9.55).

c) Synthesis of dialkyl decyl-malonate. $C_{10}H_{21}CH\overset{COOR}{\underset{COOR}{\diagup\diagdown}}$

The authors have transesterificated (I) with some fatty alcohols. A mixture of (I) (1 mole) and excess of the alcohol (4 moles) was stirred for 18 hours on a boiling water bath. Excess alcohol and unreacted (I) were distilled off under reduced pressure, and the residue was recrystallized from ethyl alcohol. The results are as follows:

Alcohol	Yield	m. p.	Saponfication value			
lauryl alcohol	85.5%	25°C.	found 175.33	calcd. 178.97
n-octyl alcohol	35%	20°C.	" 229.01	" 232.34
n-butyl alcohol	unreacteted

2. Synthesis of Some Derivatives of 2-n-Heptadecyl-indole.

As it is well known, the 3-position of indole is very reactive, but no paper has been published as yet in which ethyleneoxide was intended to react with the indol. In order to obtain a new non-ionic surfactant the authors have succeeded for first time in this reaction using 2-n-heptadecylindole.

a) Synthesis of 2-n-heptadecyl indole. (II)
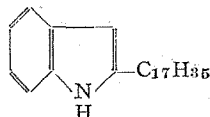
The compound (II) was obtained by heating stearoyl o-toluidine and NaNH$_2$ in N$_2$ stream referring to "Org. Synth.", Vol. 22, 94. Yield 56%, m.p. 60°C, N% 3.89 (Calcd. 3.92).

b) Reaction with ethylene oxide. The reaction product is
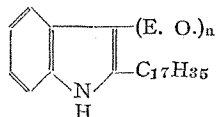
Ethylene oxide was blown into 5g. of (II) containing 5% KOH as a catalyst for 3.7 hours at 160-180°C. The weight increased to 6.9g. Molecular weight by cryoscopic method was 888. Surface tensions of water solutions were measured by Du Nouy's tensiometer. Results are (dyne/cm.) 38,9 (1%), 41.3 (0.5%) and 42.9 (0.1%).

c) Reaction with formaline.

Bis-(2-n-heptadecyl-indolyl)-methane (III) was obtained by the reaction between (II) and formaline.

$$\text{(indolyl)}-C_{17}H_{35}\quad CH_2\quad H_{35}C_{17}-\text{(indolyl)}$$
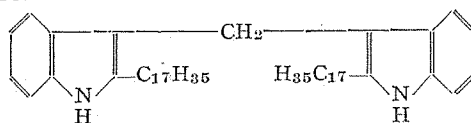
Yield 31%; m.p. 103°C.; mol. wt., 730 (calcd. 724); N% 3.81, (calcd. 3.87).

Further we tried to obtain a Mannich base from (II) under various conditions, but against expectation the product obtained was only (III).

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22. Artificial Coalification of the Mixtures of Cellulose and Lignin

Wataru FUNASAKA and Chikao YOKOKAWA

(Kodama Laboratory)

According to the Bergius' "Artificial Coalification Method", the mixtures of cellulose and lignin (in various ratios) were artificially coalified in water, $N/10$-NaOH or $N/10$-oxalic acid medium at 300°C for 6 hrs. Yields of artificial coals were measured and proximate and rational analyses were carried out.

Artificial coals, produced in water medium, scarcely showed caking power and comparatively lignin rich ones sintered strongly; on the other hand, cellulose containing (more than 40%) coals, produced in alkaline or acidic mediums, has a strong caking power.

The co-existence of cellulose and lignin results the increase in yield of produots and the increase in volatile matter or bitumen of products (in another words, bituminisation of lignin is promoted). It has been recognized, when cellulose and lignin were artificially coalified individually, very active intermediate products were formed and these polymerized easily. There may be some chemical combinations between these two intermediates, namely, the artificial coals from mixture of cellulose and lignin are not the mixtures of cellulose coal and lignin coal but partly consist of combined substances.

There are no doubts that natural coals were formed from woods through huminificating and dynamochemical actions. On the other hand up-to-date theories for coal formation scarcely have payed attentions to the relation between coal characters and chemical compositions of the starting materials for the dynamochemical stage (for example, the ratio of cellulose to lignin content of decayed wood or humus) Considering our previous works and this experimental result, it seems adequate to conclude, the complicated characters of natural coals depend considerably upon the chemical compositions of the materials, and cellulose has a great effect on the caking property of bituminous coals.