

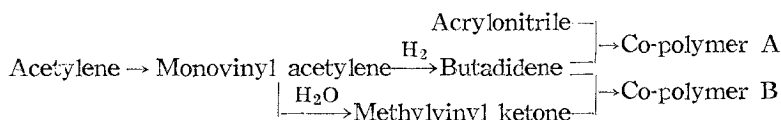
THE ODA LABORATORY

Head: Prof. Dr. Ryohei Oda

1. Studies in the Synthesis of Rubber from Acetylene

By J. Furukawa and others

This research was carried out by Mr. Furukawa and co-workers under professor Kita's direction in 1937~1943. In 1942 an industrial pilot plant was constructed in this institute, and about 50 kg synthetic rubber per day was produced, which was applied to military purpose. At the end of War II, two new industrial plants were constructed at Kurosaki in Kyushu and at Niihama in Shikoku. The method of synthesis was as follows.



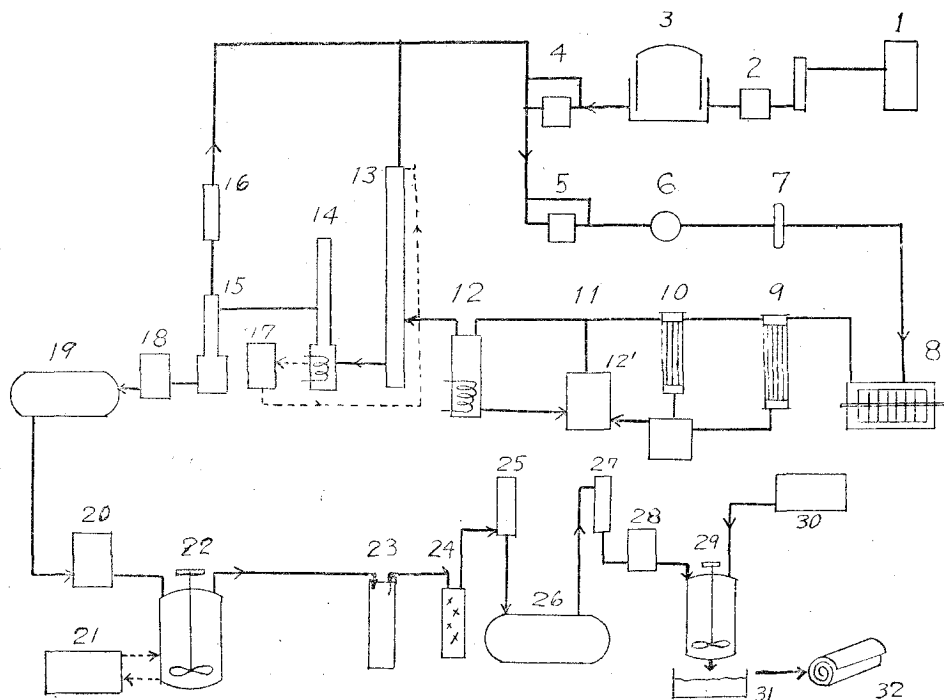
At first we studied the reaction velocity of production of monovinyl-acetylene (MVA), which was produced by polymerization of acetylene with water solution of cuprous chloride and ammonium chloride as catalyst, the so called Nieuwland-catalyst.¹⁾ It was made clear that divinylacetylene is made from MVA, and that the yield of MVA is regulated by controlling reaction time, or by varying velocity of acetylene supply and at an optimum condition the yield of mono- and divinyl-acetylene reached at 80% and 20% respectively at 25% conversion of acetylene. But the practical yield is lowered by incomplete contact of acetylene with catalyst solution, and therefore the degree of agitation is the most important factor. If α is diffusion factor of acetylene to solution, the overall reaction velocity is to be $k(1/k + 1/\alpha)$, where k is the true reaction velocity.²⁾ Coefficient α varied according to the construction of converter. Of many types of converter, we found that the horizontal rotary basket type was most effective.³⁾ This applied to an industrial plant, and gave a satisfactory result.⁴⁾ This type of converter had another advantage, i.e., it can avoid coagulation of catalyst, which was induced by contact of condensed water with catalyst solution.⁵⁾

The Separation of MVA from acetylene is one important industrial problem. Among various methods, i.e. condensation by cooling at -70°C ., absorption by solvent etc., we have adopted the absorption method. Absorption isotherm of MVA and acetylene with several solvents at various temperatures was determined, and it was determined that the use of toluene, xylene, chloroform, carbon tetrachloride at $-10 \sim -20^\circ\text{C}$ is most preferable. At low temperature the absorption ratio of MVA to acetylene is larger than at ordinary temperature.⁶⁾ Many experiments about absorption with a plate column and a packed tower at low temperature were carried out.⁷⁾

The separation of divinyl acetylene and water moisture before the absorption of MVA was necessary, which could be carried out by washing of reacted gas with

cooled brine water in pre-cooler.⁵⁾

A pilot plant with the capacity of 50 kg synthetic rubber per day was constructed in the Institute for Chemical Research at Takatsuki, which is shown in following flow sheet.^{4), 5)}



Flow sheet of synthetic rubber plant.

- | | |
|---|---|
| 1. Acetylen generator. | 18. Measuring tank for MVA. |
| 2. Acetylene dryer. | 19. Storage tank for MVA. |
| 3. Acetylene holder. | 20. Measuring tank for MVA. |
| 4. Gasmeter. | 21. Electrolytic recovery device for zink-dust. |
| 5. Gasmeter. | 22. Reduction autoclave for MVA. |
| 6. Acetylene circulating pump. | 23. Butadine washer ($\text{NH}_4\text{OH} + \text{CuCl}$ used). |
| 7. Acetylene flowmeter. | 24. Butadiene drier. |
| 8. Rotary type acetylene converter. | 25. Butadiene condenser. |
| 9. Water cooler (20°C). | 26. Storage tank for butadiene. |
| 10. Water cooler (0°C). | 27. Butadiene condenser. |
| 12. Dehumidifier (-20°C). | 28. Measuring tank for butadiene. |
| 12'. DVA Separator. | 29. Polymerization autoclave. |
| 13. Absorption column (Toluene used at -15°C). | 30. Measuring tank for acrylonitrile or methyl vinyl ketone. |
| 14. Desorption column. | 31. Coagulating tank. |
| 15. MVA Rectifier. | 32. Synthetic rubber. |
| 16. Reflux condenser for MVA. | |
| 17. Solvent tank. | |

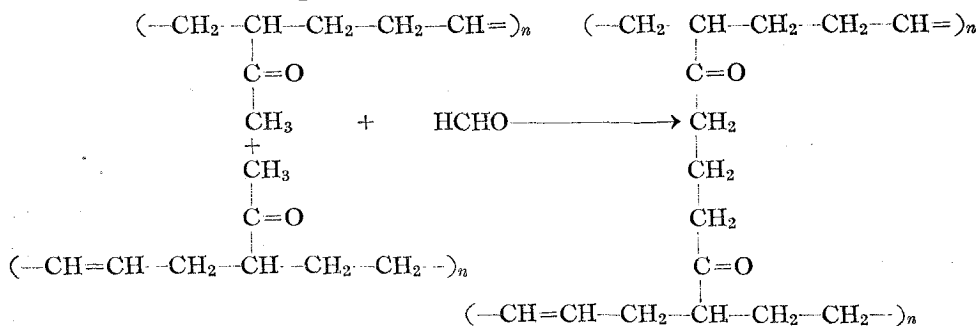
The second process, the preparation of butadiene by hydrogenation of MVA were studied. The vapor phase and the liquid phase catalytic hydrogenation with various catalyst, i. e., nickel, cobalt, iron catalyst were tested, which produced no satisfactory result except palladium catalyst.⁸⁾

An excellent method was found; using zinc dust and alkali with small amount of ferrous or cupric sulfate in autoclave, pure butadiene was obtained with practically quantitative yield.⁹⁾ Zinc used, which converted into sodium zincate solution was recovered by the electrolytic method, and it was capable to use again in wet spongy state for next hydrogenation. And a direct electrolytic reduction of MVA was also applicable by using nickel cathode and zinc anode.¹⁰⁾

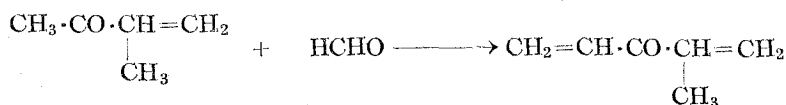
The butadiene obtained by this method is very pure and contains at most 0~2% MVA, but no butene. The removal of MVA from butadiene was successful by washing crude butadiene gas with ammoniacal solution of cuprous chloride and ammonium chloride or of silver nitrate.¹¹⁾

The neutral solution of cuprous chloride precipitated not only MVA but also butadiene as shown in the literature. In ammoniacal solution, on the contrary, MVA was precipitated, but butadiene remains in solution.¹²⁾ The non-corrosive character of ammoniacal solution of cuprous chloride is advantageous for technical apparatus.

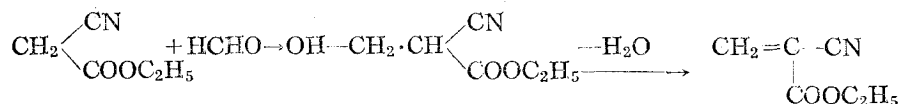
The analytical method for crude gas of MVA synthesis and butadiene synthesis was established.¹³⁾ The third process, polymerization of butadiene to synthetic latex was studied both theoretically and practically. A new synthetic rubber was made by co-polymerization of butadiene and methyl vinyl ketone.¹⁴⁾ The latter was prepared in an economical way from MVA by gaseous phase catalytic hydration with phosphoric acid catalyst.¹⁵⁾ This synthetic rubber has good workability, anti-aging character and resistivity. It can be vulcanized with sulfur by an ordinary method and also with hexamethylene-tetramine without sulfur.¹⁶⁾ The methylene bridge will probably take place by reaction between formaldehyde and ketone group of rubber as the following scheme shows:



We obtained a new divinyl compound (b. p.₁₀₀ 45~46°C n_D^{22} 1.43024, d_4^{20} 0.8727) by reaction of formaldehyde and methyl iso-propenylketone, which had ability of polymerization.¹⁷⁾



A certain new polymerizable compound i. e. cyano-acrylic ester (b. p. 52, n_D^{20} 1.4432 d_4^{20} 1.1152) was prepared, and co-polymerized with butadiene.¹⁸⁾



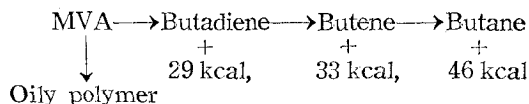
Butadiene-acrylonitrile co-polymer was manufactured industrially for military purpose at Takatsuki and the end of the War at the Niihama and Kurosaki factories.

Theoretical research on the mechanism of emulsion polymerization¹⁹⁾ and co-polymerization were carried out.²⁰⁾ The theory of co-polymerization introduced independently by the author coincided with that revealed in the other scientific literature received after the war.

2. Preparation of butylene from M.V.A.²¹⁾

By J. Furukawa, N. Ikariyama and others

A study in the preparation of butylene as an intermediate product for iso-octane was carried out in 1943~1944. Partial hydrogenation of MVA to butene is difficult for the reason of by-production of butadiene and butane as shown in the process below. Among various catalysts we preferred nickel from an industrial viewpoint.



In liquid phase hydrogenation, velocity of hydrogenation of MVA to butene is influenced by reaction temperature and pressure. Velocity is accelerated 1.8 fold at every 10°C while 1.63 fold at every 16 atmospheric pressure at ordinally temperature. The hydrogenation velocity of intermediate pure components were determined as seen in the following table.

	Temperature at which hydrogenation takes place °C	Hydrogen absorbed, cc/min.
MVA	17	35
Butadien	25	153
Butene	34	19

But in hydrogenation of MVA to butene as the result of anylysis of intermediate in various reaction times the ratio of hydrogenation velocity of intermediate did not agree with the data given above, while was to be 1:0.66:0.2 (MVA:butadiene:butene). This fact will be due to greater ability of adsorption of MVA on catalyst than butadiene. MVA polymerized to oily polymer simulutanously in hydrogenation, which lowered the activity of catalyst. Hydrogenation and polymerization are conquerent reactions, the ratio of which is 1:0.43. The mean capacity of catalyst is about 150 gr. MVA per 1 gr. nickel. This oil, which is probably a hydrogenated dimer of MVA, is available as crude material of lubricant oil, which is prepared by polymerization with aluminium chloride or as the source of butene, regenerated by thermal cracking of oil with silica gel as catalyst.

The gaseous phase hydrogenation of MVA to butene with nickel catalyst was realized in a large scale pilot plant with capacity of 50 kg per day. Excessive hydrogenation was avoided by using catalyst diluted with a large amount of carrier mass or by using catalyst partially poisoned with sodium sulfide or lead ion, or by controlling of reaction time or gas velocity, and the most profitable method was established by dilution of reactant gas with water vapor, which is 4~7 volume per 1 volume of MVA, especially used at the initial time of reaction (1 or 3 days).

An example of reaction is as follows: In iron tube with 2" dia, and 90 cm length inserted 100 g catalyst (nickel: kieselgel=10:100) and 150 g pumice stone in 25 cm length into which mixed gas at the rate of 30 l. per hr. of MVA, H₂ and H₂O (1:4:8), was introduced for the time of 30 days. The yield of butene reached at about 70 to 90% without butane. Distribution of conversion and temperature in the reaction tube are examined and discussed theoretically. The activation energy calculated from temperature coefficient of overall reaction velocity is about 7 kcal/mol.

3. Studies in the Plasticity, Elasticity and other Physical properties of Rubber and High Polymers

By J. Furukawa, K. Tomihisa, M. Nishida and M. Asai

After the War, our efforts were turned to physico-chemical research of rubber and other high polymers. Measuring the velocity of deformation of unvulcanized rubber with Goodrich's plastometer, we evaluated plastic viscosity and its temperature coefficient or its change with the molecular weight of rubber. It was found that the log-log plot of softness and plasticity gave a linear relation in linear polymer, on the contrary non linear in cross-linked polymer, i. e. some synthetic rubber or reclaimed rubber. The logarithmus of fluidity φ is linearly related with reciprocal absolute temperature T , i. e.

$$\log \varphi = A + E/RT$$

In the case of visco-elasticity A and E increase with molecular weight.²²⁾ The fluidity of mixture of rubber with different degree of molecular weight is represented strictly neither in number average nor in weight average, but in segment-average.²³⁾

Our research was extended to problems on the mechanism of reinforcement of filler. Filler decreases the fluidity of rubber, and increases the elasticity and mechanical strength of vulcanized rubber. We submit that rubber adsorbed on filler and were united mutually. Regarding filler-rubber mixture as the system of rubber and block of rubber, its fluidity was calculated theoretically as seen in the following.²⁴⁾

$$\ln \varphi_0/\varphi = (a+b/RT) \cdot (1+SM/Na) \cdot X$$

where φ and φ_0 are fluidities of pure and filler containing rubber, respectively, X is the volume ratio of filler to rubber, S is the specific area of filler, N is Avogadro's number and a , b are constants, and coefficient a is the effective contact surface of filler. Based on this theory, the logarithmus of fluidity will increase proportionally with filler content X , and linearly with the specific surface of filler and the molecular weight of rubber used. Our experiments were fairly consistent with this theory. The area of contact point a is 26 Å² from experiments varied with molecular

weight of rubber or with specific surface of filler.

In the case of vulcanized rubber the filler is united with rubber molecules in the same manner with the cross-linking caused by vulcanization. The elasticity of sample with filler, E is theoretically put down as follows:

$$E = E_0 + SXRT/a$$

where E_0 is the elasticity of rubber without filler, which agreed with the results of experiment.

Our next research related with the strength of vulcanized rubber. In Flory's theory, the strength of vulcanized rubber depends on the concentration of effective closed chain except free terminal chain, which is put down as $(1-2N/M\nu)$, where M is the molecular weight of original rubber before vulcanization, ν is number of cross-linkage per unit volume, N is Avogadro's number, and tensile strength at break τ is put down as follows.

$$\tau = K(1-2N/M\nu)$$

This equation agreed with experiments so far as the molecular weight of original rubber was concerned while it could not represent the existence of the maximum tensile strength with regard to the degree of vulcanization, which occurred in fact. Regarding that cross-linking not only increases the concentration of effective chain, but also renders hindering action on crystallisation, when the rubber were stretched. From such an interpretation, we obtained the following equation:²⁵⁾

$$\tau = \frac{K}{M_0} \left\{ (1-2N/\nu M) - \beta \nu \right\}$$

where K is the strength caused by one isoprene unit M_0 and β is coefficient with regard to the effect of hindrance to crystallisation on stretching caused by one cross-linking. It has the maximum value as to degree of cross-linking, which was obtained by putting $(\partial\tau/\partial\nu)$ to zero, i.e.

$$\begin{aligned} \nu_{max} &= N \sqrt{\frac{2}{MM_0\beta}} \\ \tau_{max} &= K \frac{N}{M_0} \left\{ 1 - 2\sqrt{\frac{2\beta M_0}{M}} \right\} \end{aligned}$$

It requires that ν_{max} and τ_{max} are in linear relation with M , which fairly agreed with experiments from which the author calculated the value of K equal to 400 kg/cm² and β equal to 10, respectively.

We made also a study of the vulcanization of rubber, especially of its reaction velocity.²⁶⁾ It is of interest that the number of sulphur cross-linking calculated from the limit of vulcanization is not equal to the number of cross-linking calculated from its elasticity, the former being about 4 times larger than the latter. The cross-linking seems to consist of complex polysulfide binding.

We are interested in the action of scorch retarder, for instance *N*-nitrosodiphenylamine.²⁷⁾ From experiments with the Mooney-plastometer, it was made clear that it acts as the inhibitor like hydroquinone in vinylpolymerization as shown in the following:

we have obtained hexenal or octenal from acetylene and water under pressure with about 60% yield. Various experiments with compressed acetylene are being continued.³⁸⁾

Some experiments on the vinyl-exchange reaction or ionic polymerization of vinylacetate or vinyl ether have been also reported by author.³⁹⁾

6. Research on Ion Exchange Resins

By R. Oda and H. Shimizu⁴⁰⁾

Since 1943 we have been engaging in the research of ion exchange resins. Principal efforts were directed at first to the preparation of various kinds of ion exchange resins. Some resins prepared in our laboratory are as follows:

Mark Materials and manufacturing method.

KH-1 Sulfonation product of natural rubber-SO₃H-type cation exchanger.

KH-4 Condensation product of phenoxyacetic acid with the formaldehyde-COOH-type cation exchanger. This resin was prepared under special precaution with the aim to make it fit for the microdetermination of vitamin B₆. Amberlite IRC-50 can not be used for this purpose, because resin itself eludes a certain component, which combines with 2,6-dichlor-quinone-imine chloride.

KH-6 Condensation product of resorcino-oxydiacetic acid with formaldehyde-COOH-type cation exchanger.

KH-9 Condensation product of phenol-sulfonic acid with formaldehyde-SO₃H-type cation exchanger.

This resin was also prepared under special precaution with the aim to make it fit for the microdetermination of vitamin B₂. Amberlite IR-120 can not be used for this purpose, because resin itself eludes some fluorescent components.

AH-8 Condensation product of 2-amino-4-methylthiazol with formaldehyde-NH₂-type anion exchanger.

This resin is partially soluble in dilute mineral acid like many other basic resins. Ambertlite IR-4B is also partially soluble in mineral acid. We prepared a special insoluble resin which was absolutely insoluble in mineral acid, by condensing a mixture of 2-amino-4-methylthiazol and phenol (10% in mole ratio to 2-amino-4-methylthiazol) with formaldehyde.

On the application of ion exchange resins we have performed successful experiments mainly on the following items:

- 1) Preparation of pseudo-distilled water.
- 2) Deionisation of sea water.
- 3) Softening of hard water.
- 4) Removal of F⁻ ions from drinking water, using HCl-salts of basic resin.
- 5) Concentration of Vitamin B₁ from its extract.
- 6) Microdetermination of Vitamin B₆, using the above-mentioned KH-4 as absorbent.
- 7) Microdetermination of Vitamin B₂, using the above-mentioned KH-9 as absorbent.
- 8) Use of acidic resins as chemical catalysers.

Items (4), (6) and (7) were performed quite independently, and excellent results were obtained.

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THE SASAKI LABORATORY

Head: Prof. Dr. Nobuji Sasaki

On the Formation of Powder

For last several years our laboratory carried out research of the morphological changes of substances caused by chemical and physical treatments. We studied chiefly wolframic oxide and metallic wolfram powder by employing optical and electron microscopes, X-ray diffraction, a quartz-fibre spring-balance as well as using the BET adsorption method.

1. Precipitated Wolframic Acids

Wolframic acids or wolframic oxide hydrates made by decomposing aqueous solutions of wolframates with mineral acid are known in three different colors, yellow, white, and green, probably due to different contents and different modes of combination of water.

Electron microscopic observations were made with wolframic acid crystals obtained by the decomposition of a sodium wolframate solution with hydrochloric acid under different conditions. The decomposition at 25°C yields a white precipitate consisting of 1-2 μ thin crystals of various shapes, such as a disc, halfmoon, boat, and polygon. The decomposition at a higher temperature (80°C) gives a yellow precipitate consisting of ca. 0.05 μ thin, generally angular crystals, which, though finer than the white one, precipitates faster than the latter. The part of the white precipitate which resists centrifugal precipitation, consisted of ca. 0.1 μ needles and ca. 0.2 μ particle of indefinite shape, which grow slowly to a network and strings of beads of different lengths, respectively. The dehydration-temperature curve obtained by means of a quartz-fibre spring-balance shows, with the white precipitate, a monotonously falling curve ending in the composition of WO_3 at ca. 300°C, while, with the yellow precipitate, the curve has a horizontal part extending from 85 to 185°C, which corresponds to the composition of $\text{WO}_3 \cdot \text{H}_2\text{O}$. This fact indicates the differences in the state of the combination of water of hydration. WO_3 particles obtained by dehydration are roughly of the same size (ca. 0.02 μ), independent of the condition of the formation of wolframic acids, their shape and size, and the manner of dehydration.

2. Decrease in the Surface Area of Wolframic Oxide Powder by Heating

Wolframic oxide powder is generally made by the dehydration of wolframic acid, which is complete at about 300°C. The fine powder thus obtained grows in size on heating at higher temperatures. The change in the total surface area of various powders when heated in air and in vacuum at 500-900°C was measured by the BET method with especial regard to the effect of the doping materials (K_2SiO_3 , Al_2O_3 , and KCl) added to the powders. The decrease in the surface area is greater, when the heating temperature is higher, for instance, with pure WO_3