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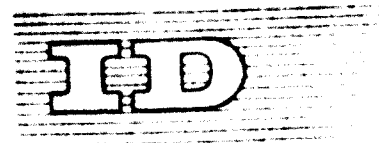
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21

PROCESSES OF POLYMERIZATION AND
ISOPRENE RUBBERS

6.

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USSR

THE SOVIET METHOD OF MANUFACTURING OF ISOPRENE AND POLYISOPRENE RUBBER BASED ON ISOBUTYLENE AND FORMAL- DEHYDE

INTRODUCTION

Complex investigations aimed at working out the methods for isoprene synthesis and obtaining isoprene rubber were started in the USSR in the fifties.

At present the main commercial methods for isoprene synthesis are the following:

- a) from isobutylene and formaldehyde (dioxan method);
- b) decomposition of isopentane and isobutylenes;
- c) from isopentane through the stage of its dimerization;
- d) from isobutylene and formaldehyde (Zaverzky method);
- e) isoprene as a by-product of polyisole fraction.

Table I summarizes the data given by G. B. Litvin, K. S. Solov'ev and M. A. Zaverzky concerning relative production cost, proportion of capital investments, and energy consumption in the manufacturing of isoprene by different methods. In spite of some relative error of the calculations, as well as the dependence of their results on the price of the raw material which is determined by local conjuncture, while analyzing this Table one can draw certain conclusions concerning the relative economy of the above mentioned methods.

First of all the basic characteristics of the four main methods are near enough. So, the differences in the calculated isoprene production costs do not exceed 20-25 per cent. The dif-

ferences in proportional capital investments and energy consumption are more vivid. Based on these characteristics the methods of isopentane dehydrogenation and acetylene through propylene dimer are considered to be less economical.

Table 1. Correlated technical and economical characteristics of different methods for isoprene production

No.	Method of production	Proportional capital investments (with regard to feed and energy sources)	Production cost	Energy consumption
1	From isobutylene and formaldehyde: a) in the production of isobutylene by isobutane dehydrogenation b) using isobutylene containing in C_4 fractions of pyrolysis and cracking	100 100	100 85	100 100
2	Isopentane dehydrogenation by two-stage flow diagram	180	119	120
3	From propylene through its dimer	102-112	89-111	141-150
4	From acetylene and acetone	94-130	96-111	72-100

On the other hand, as can be seen from the table, the dioxan method is, on the whole, much more successful as compared to the other methods. It is worth mentioning the advantages of this method as well as raw material availability, and great differences in essentialities are taken into account, it becomes evident that the dioxan method possesses rather big technical prospects.

The development of directed stereospecific isoprene polymerization using alkylaluminum halides and Ziegler-Natta catalysts has proved to be an outstanding achievement in chemistry of polymers.

The use of the above said catalysts made it possible to work out conventional methods for the synthesis of cis-1,4-polyisoprene, which possesses practically the same structure as natural rubber.

The great increase in the production of stereoregular rubbers is taking place in the present years in various parts of the world. The data on the world annual production of synthetic polyisoprene since 1961 till 1964 are given in Table 1. The USSR is not included. It is seen from the table that the world annual production of polyisoprene rubber is now only 52 thousand tons, while by 1964 it is to amount to 59 thousand tons, that is to increase in 10 years for more than 10 times.

Table 1. The world annual production of synthetic polyisoprene rubber (the USSR is not included)

Year	Total output, thousand tons/year
1961	5.0
1962	10.2
1963	53.4
1964	59.0

I. Isoprene Synthesis

A brief description of isoprene synthesis based on isobutylene and formaldehyde, commercially first realized in USSR is given below.

Interaction of olefins with formaldehyde yielding in cyclic formals - dioxans (Prins reaction) forms the basis of the process.

Through analytic cracking of dioxans the corresponding diene hydrocarbons are formed.

During a long period of time many specialists considered the dioxan method to be not promising due to the comparatively low selectivity of the Prins reaction and the complexity of the flow diagram. So, for example, respected research workers Brundale and Mikeska, discussing the possibility of commercial production of dienes by Prins reaction wrote: "... in view of the low yields, diolefin synthesis by the above method (from isobutylene and formaldehyde, etc.) would not appear particularly attractive unless such diolefins could not be produced by other means." (Mikeska J. A., Brundale E. Chem. Revs., 51, 505 (1952)). However, the commercial experience showed that the dioxan method is able to become one of the main commercial isoprene syntheses in case the regularities of the process are thoroughly investigated and the engineering problems are solved the right way. The methodical and technical bases of the process have been investigated in the USSR by M. I. Farberov and M. S. Nemtsov starting with the end of the forties.

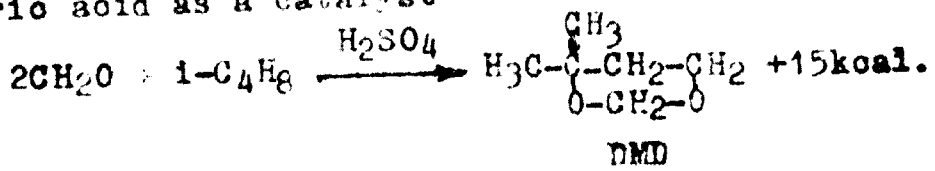
²The USSR also possesses operating commercial units for manufacturing isoprene by isopentane dehydrogenation.

In 1954 a semi-commercial unit for manufacture of isoprene from isobutylene and formaldehyde was in operation in the USSR, at which the basic technological parameters were worked out and large lots of the product were manufactured. In future a project of two plants producing isoprene and isoprene rubber was designed as a result of the joint work of the research institute and the designing organization. The both plants were put into operation by the end of 1960. The basic technological elements of the Soviet process have been patented in the mostly highly developed countries.

Parallel to the Soviet research work to design the dioxan method for isoprene synthesis, French Institute of Petroleum (IFP) have been fruitfully working at the same problem. It is seen from the papers issued by the Institute that many of the important technological elements of the French synthesis differ greatly from the Soviet ones. The process of the French Institute has been tested at a semi-pilot unit. This process also possesses several patents in the main industrial countries. The French research workers have investigated the basic regularities of the process, especially its first stage.

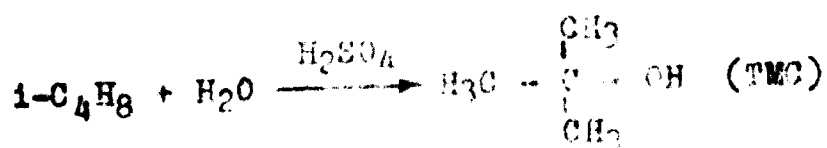
The Chemistry of the Process

The first stage of the process is the interaction of isobutylene with formaldehyde resulting in 4,4-dimethyltetrahydro-2H-pyran-1,3-dione (DMD). It proceeds at a temperature of 85-95° in the presence of sulphuric acid as a catalyst

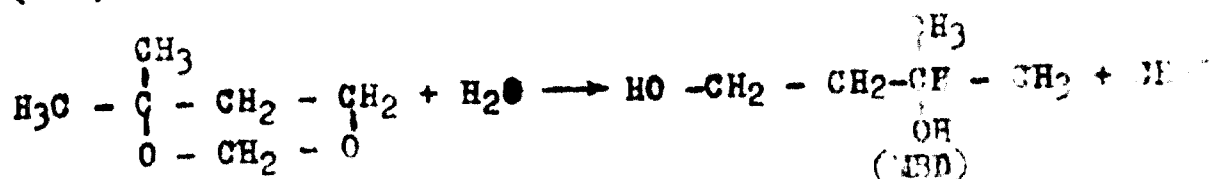


On account of the high reactivity of the components, alongside the main reaction a whole number of side reactions take place as well:

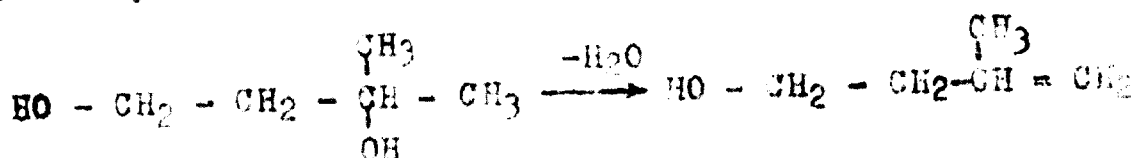
a) Isobutylene hydration yielding as the tertiary butyl alcohol - trimethylcarbinol (TMC).



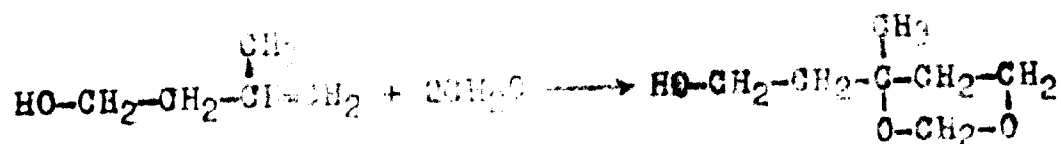
b) Reversible DMD hydrolysis resulting in 3-methylbutene-2,3 (MBD).



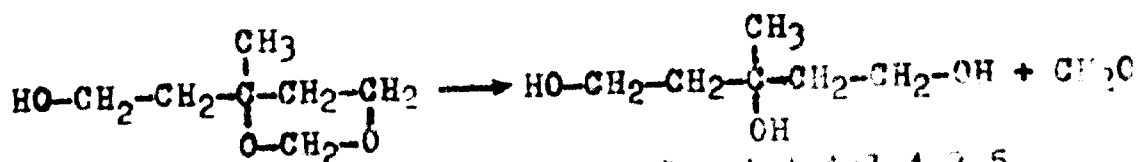
c) MBD dehydration resulting in the formation of three isomeric isoamylene alcohols. For example:



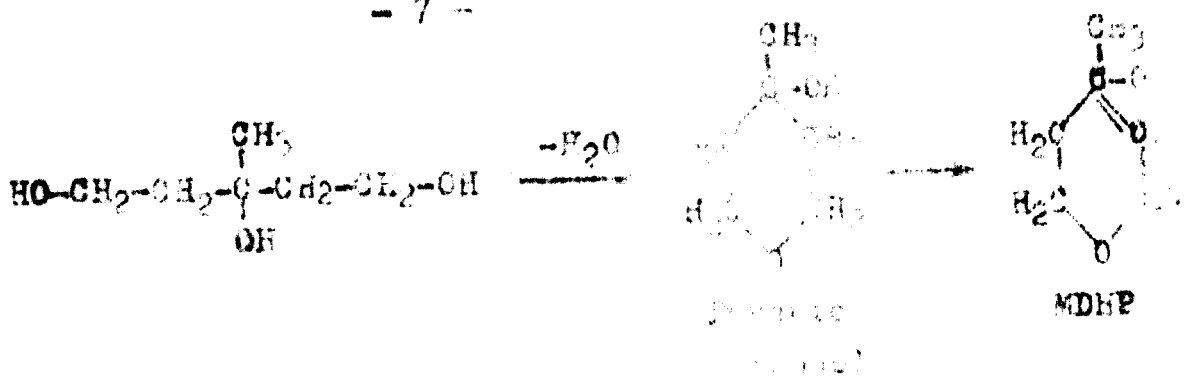
d) Interaction of unsaturated alcohols with formaldehyde resulting in three isomeric diols, for example:



e) Hydrolysis of diuran alcohols with the formation of three-atomic alcohols:



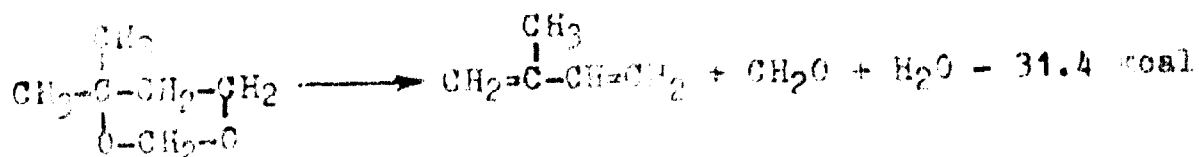
f) Triol dehydrocyclization to form pyranic alcohol which being subjected to dehydration yields in methyl dihydropyrane (MDHP).



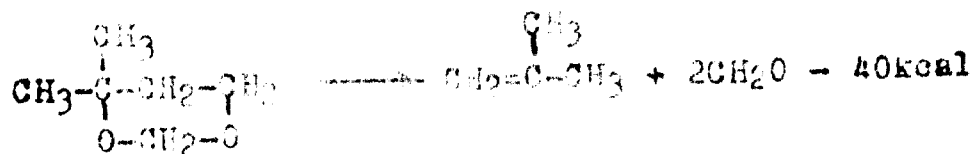
On the whole more than 60 components have been detected in the reaction mixture.

The selectivity of the main reaction relative to formaldehyde amounts to 75-80%, and relative to isobutylene is 68-70%. TMO, MBD, dioxane alcohols and their derivatives predominate among the by-products.

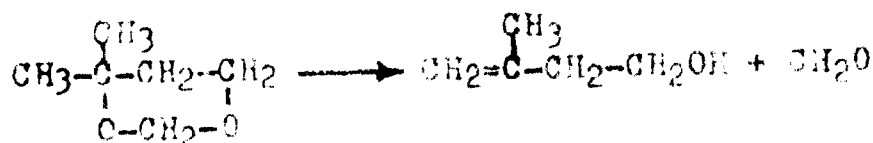
The second stage of process - the selective decomposition of 4,4-dimethyltetrahydro-2H-pyran resulting in the formation of isoprene - proceeds in the vapour phase on the heterogeneous catalyst (a mixture of acid and medium calcium phosphates).



The main side reaction is the DMD cracking into isobutylene and formaldehyde (the reaction is in parallel to the main reaction of the first stage).

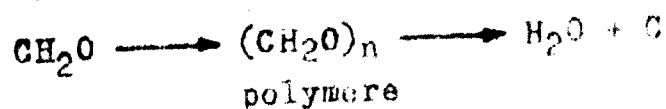


Isobutenyl carbinole, also formed from DMD is usually present in the catalysates of the second stage as well:

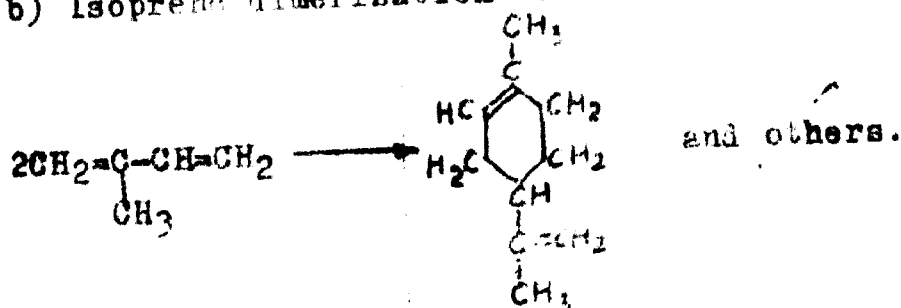


Alongside the above listed reactions the following side reactions proceed as well:

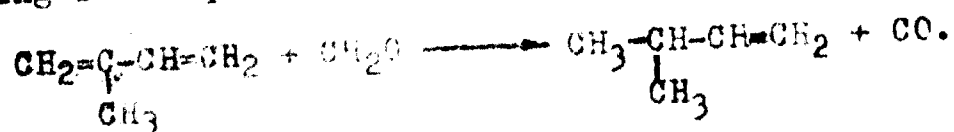
a) Formaldehyde decomposition



b) Isoprene dimerization to form terpenes ("green oil")

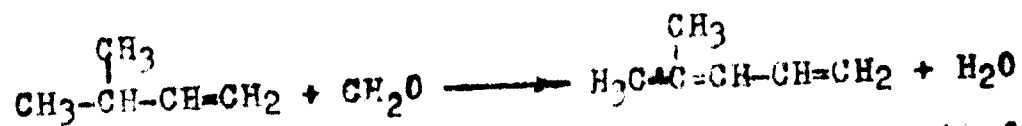


c) Hydrogenation of isoprene at the cost of formaldehyde, forming small quantities of amylenes. For example:

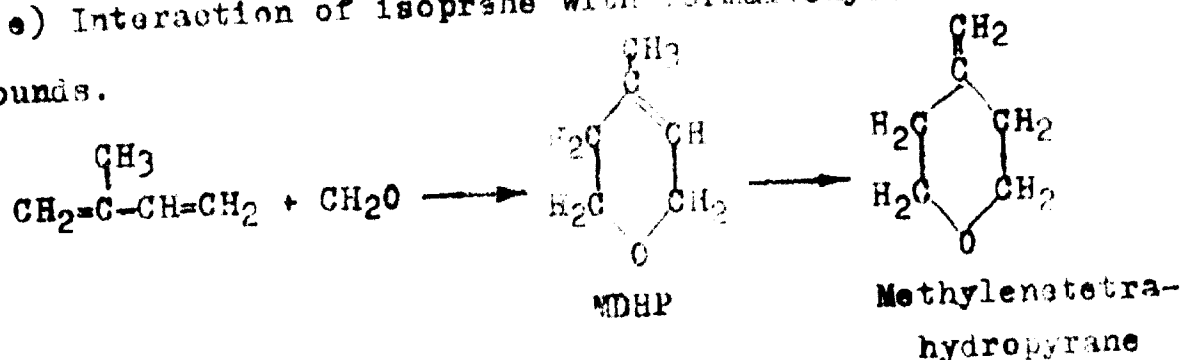


d) Further interaction of amylenes with formaldehyde to form hexadienes.

For example:



e) Interaction of isoprene with formaldehyde to form pyrane compounds.



The selectivity of the main reaction relative to isoprene amounts to 82-83% and relative to isobutylene - about 10%.

A Brief Description of the Flow Diagram

The starting raw material - formaline, being deprived of methanol, containing 1-1.5% of sulphuric acid, and liquefied C₄

section, containing isobutane* - and isobutene, arranged in two series - parallel to each other. The reactors operate in a series of spray columns (C_4 -fraction is sprayed), which affords sufficient mixing of the two phases. Each reactor has a jacket through which water at a preset temperature is passed. The two-reactor system makes it possible to obtain rather high conversions of the both reagents (up to 90-93%).

The reaction liquid consists of the two phases as well: water and organic. Processing of these phases proceeds at two different technological lines. The organic phase, being washed with water off dissolved formaldehyde and sulphuric acid, enters the rectifying columns block, where DMB is separated from more volatile and more heavy impurities.

The water phase passes through the sulphuric acid neutralization stage. After this it is distilled off the mixture of DMB and of other "low-boiling" impurities, which are removed, and then the water phase is distilled off the unreacted formaldehyde. The high-boiling impurities dissolved in water liquid are separated from this liquid, (by extraction, for instance), and the residue is directed into the sink system.

The cracking of diethyldioxane-rectificate proceeds in column-type reactors.

The delivery of the required amount of heat is carried out by introducing the overheated steam into each section.

In order to maintain the catalyst activity, small quantities of phosphoric acid are introduced into the reaction zone.

* C_4 -fraction of different origin (of isobutane dehydrogenation, cracking, pyrolysis and others) can be utilized for DMB synthesis.

The process comprises the two alternate cycles: that of contact and regeneration.

DMD evaporation proceeds in the flow of vigorous steam in the evaporator. Then the charge is overheated, diluted with steam and introduced into the first reactor section. During the contact period the temperature in the reactor section is held in the range from 330° to 400°C, accompanied by the introduction of overheated steam.

Due to coke deposition on the surface of the catalyst, the activity over one cycle somewhat lowers.

The catalyst regeneration consists of coke burning in the stream of air, diluted with water steam.

As a result of contact gas condensation one obtains the reaction liquid consisting of two phases: organic and water. The organic layer, being washed off from aldehyde, is introduced into the rectifying column where isobutylene is separated from isobutylene and more "heavy" products. The obtained raw isoprene is subjected to more complete refining.

The fact that isoprene is usually not accompanied by close-boiling compounds (as, for instance, in the process of isopentane dehydrogenation) is a characteristic feature of the process. As a consequence it is comparatively easy to obtain directly the monomer of high purity. The water layer, containing formaldehyde, DMD, unsaturated alcohols, methylidihydropyrane and small amounts of other organic products is processed at an independent technological line.

Unreacted DMD, containing isocamylene alcohol is recycled. Isobutylene and formaldehyde obtained as a result of cracking are returned to the first stage.

Table III lists the typical qualitative characteristics of technical grade isoprene-rectificate.

Table III

No.	Component	Weight per cent
1	Isoprene	99.6 - 99.8
2	α -Isoamylene	0.15
3	β -Isoamylene	0.12
4	γ -Isoamylene	0.063
5	Isobutylene	0.012
6	Carbonyl compounds	0.00025
7	Cyclopentadiene	0.00007
8	Acetylenic compounds	0.00013

Utilization of the By-Products

The major part of by-products are formed in the first stage of the process - in DMD production. The main part of by-products in DMD synthesis consists of high-boiling (b.p. > 200°C) oxygen-containing compounds - one, two and three-carbon alcohols, linear and cyclic ethers and so on (see above). The quantity of these products amounts to 20-24 kg per 1 ton of DMD, based at 1 ton of isoprene-rectificate (this figure increases to 430-450 kg. Thus, the solution of this problem concerning the qualified utilization of high-boiling by-products amounts almost to a half of the obtained isoprene, and could substantially improve the economy of the process as a whole.*

*It should be stressed again that the main characteristics of the process given in Table I are estimated with no regard to the possibility to use the by-products.

... to the chemical nature of the products in question. The main trends of their utilization seem to be the following:

1. The utilization of close-boiling individual products or groups of them in intermediate and final stage syntheses including, for example, solvent production and so on.

2. The use of high-boiling technical mixtures as solvents, reagents, catalysts, and so on.

3. The use of high-boiling technical mixtures as feedstocks for the production of isoprene and starting materials for isobutylene.

The realization of the first direction has met a number of difficulties.

The separation of individual compounds or at least close-out fractions, and the removal of these compounds from technical mixture has proved to be a rather complicated and expensive operation. These mixtures contain up to 50-60 close-boiling compounds, many of which are thermally unstable. The separation of the above-mentioned compounds is difficult even in high vacuum. It is rather difficult to find out the possibilities to use the fractions obtained in quantities comparable with its potential output. In this connection, we have found variants to use some components. For example, MBO may be used as raw material in isoprene production or in the production of some vitamins. Numerous attempts to find a complex solution of the problem of no success are present.

The trend of utilization of high-boiling by-products has been developing with a much greater success. It was found that the recovery of isoprene, recovering from the organic layer of the reaction mixture. DM synthesis can be used in mining as a feed-

tating reagent - a reducing agent - increasing the alloy ore. One thousand tons of the ore is already utilized this way in the USSR industry. It has been also demonstrated that wide-boiling cuts of high-boiling by-products can be utilized as a component of phenol-formaldehyde and polyester resins. However, owing to different reasons these works have not yet found any commercial utilization. On the whole, taking into consideration the volume of production of by-products and possessing the tendency to increase this volume in future (at the expense of constructing new plants), the second trend cannot yet solve the problem as well.

One should also keep in mind the fact that through improvement in DMF synthesis the consumption of the technical product will change and it will probably take on proportions with considerable consumption and utilization.

Many experiments have been carried out in order to utilize the by-products of the process within the boundaries of the basic process. Obtaining some of the products of isoprene and at the same time releasing some of the expended raw material. It is evident that this trend does not exclude the possibility to use some part of the product in other branches of industry. However, when utilizing chemical processing of by-products it is not absolutely clear how to use the main "surplus" amount of the product. Several methods for processing of mixtures of by-products have been developed in the USSR. According to one of them wide-boiling technical mixtures undergo etherification. In the final analysis utilization of the mixture will allow the isoprene production to increase 5-10% accompanied by 5-10% decline in formaldehyde consumption, and 1-2% decline in styrene consumption. The above process was tested on a pilot plant.

In isoprene production comparatively small amounts of products are also formed - methylal, methyl tertiary butyl methyldihydroxyacetone, etc. Methods for their processing have also been worked out. In this case about the relative quantities of these products the problem of expediency of their chemical processing will be solved depending upon the corresponding units. Under certain circumstances it is reasonable to burn some technical fractions.

II. A Method for Manufacturing of Stereoregular

Isoprene Rubber SKI-3

Manufacture of SKI-3 carried out as a continuous process comprising the following steps:

- isoprene polymerization in the organic solvent medium in presence of a stereospecific catalyst;
- stopping the polymerization with alcohol;
- water washing and removal of the polymer;
- introduction of an antioxidant;
- water degassing;
- recovery of the mbis rubber crumb;
- rubber drying in band one or three stroke driers and worm apparatus;
- refining of the recirculated solvent.

The solvent and the monomer used in the process are characterized by their high purity and contain microimpurities (carbonaceous and other compounds) in amounts not exceeding 0.1% (See Table III).

The continuous polymerization is carried out in a reactor consisting of 4-5 apparatus having scraper mixers intended to clean the walls from the polymer. The isoprene concentration in the charge is about 1%, conversion degree 90%, polymer

time 2Y2 - 3 hours, temperature of the process 20-40°.

Stopping - decomposition of the catalyst - is carried out with alcohol (methanol or ethanol) which facilitates washing of aluminium and titanium salts with water in a counter-flow column. The stabilized polymer is degassed with water steam at the temperature of 95-105° in a two-stage system that yields in rubber crumb suspension (pulp) in hot water. The crumb is washed with water, wrung out and dried in band driers with air at temperatures of 100-140° during 7/8-1 1/2 hours or in worm apparatus at temperatures of 165-175° for 2-3 minutes.

The solvent distilled off as the steam by water degassing is condensed, is washed with aqueous alkali solution and water, dried by azeotropic distillation and used to prepare the charge.

Table IV. Consumption of raw and auxiliary materials per 1 ton of CYI-B

Materials	Unit	Consumption
Isoprene	kg	1020.0
Solvent	"	70.0
Aluminium alkyl	"	7.0
TiCl ₄	"	7.0
Neozon D	"	5.0
Diphenyl paraphenylene diamine	"	3.0
Technical grade stearine	"	13.0
KOH	"	10.0
NaOH	"	0.6
Electrical energy (with no regard to cold)	kwh	432.4
Cold	kg	0.512
Steam	"	9.397

(continued on the next page)

Table VI. (Continued)

Materials	m. u.	Consumption
Recycling water	"	451.1
Softened water	"	20.2

Since in foreign literature there is no data on the technological and technical characteristics of isoprene rubber production (1967 year design, USSR), it is possible to measure from the economic point of view only the rubbers SBR and SKI-3.

A comparison has been done based on the design data of SNAM Icaratti Company (Italy) and the French Institute of Technology.

Table V. Expenditures per 1 ton of rubber (USSR - design data, Italy - design data given by USSR)

Materials	m. u.	USSR	Italy
1. Rubber	t	1.02	1
2. Thermal energy (total)	kwh	800	900
3. Steam	t	16	
4. Water	m ³	500	6

(Chem. Eng., 74, 206-208 (1967))

Table VI. Expenditures per 1 ton of rubber (USSR - analog) figures, France - design data given by the French report from the Paris conference.

Items of expenditures	USSR	France
1. Isoprene	50	47.0
2. Chemicals and catalysts	14	14.6
3. Energy consumption	7	8.1
4. Wages, amortization, taxes and others	19	29.5

Europ. Chem. News, 10, No. 243, 27 (1966)

— " — , 10, No. 243, 44 (1966)

— " — , 10, No. 243, 44 (1966)

— " — , 10, No. 244, 34 (1966)

Thus in expenditures per 1 ton of rubber and the corresponding of the production cost production of SKI-3 in the USSR is on the same level as the design data given by Italian and French companies. And besides that, expenditures for isoprene polymerization and polymer recovery account for 40 per cent of the plant production price, while in France this figure is supposed to amount to 52.2 per cent.

One should take into consideration the high cost of substituted antioxidants which is absolutely unjustified from the economic standpoint and accounts for 5 per cent of the production price.

Substitution of antioxidants, modification and improvement of catalytic systems, lowering of solvent losses, ethanol recovery and other measures will allow in the near future to reduce 10 per cent out in the production price of SKI-3 rubber.

Large potentialities for cutting the isoprene production cost, as it has already been mentioned above, reside in utilizing the by-products of its synthesis.

x x

x

Scientific-research and designing institutes as well as plants have been carrying out a great amount of work directed at the further improvements in the technology and technical and economic characteristics in the manufacture of isoprene and polyisoprene rubber.



We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards, even though the best possible copy was used for preparing the master fiche.



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