

THE TECHNICAL AND ECONOMIC INTERFACE OF SYNTHETIC AND NATURAL RUBBERS

By

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Ladies and gentlemen, the first slide is, I believe, familiar to you all — the significance, quite rightly for this week, is Sri Lanka (Ceylon) at the centre of the world, as it celebrates 100 years of its rubber industry. I am proud and pleased to have received an invitation to present a lecture at these celebrations. I am also grateful for the opportunity to visit this beautiful country and meet old friends and new acquaintances.

I must admit to being a little apprehensive however, as a prominent representative of the Synthetic Rubber industry. I have the feeling that many people in the Natural Rubber business view those from the synthetic side as rather shady characters whose sole purpose in life is to erode the Natural Rubber market with a multitude of new synthetic materials.

The record however shows that this is not really true. There seems to be a fairly peaceful co-existence between god-made rubber and man-made rubber. It has meant that materials best suited to a particular application can be used. This results in greater safety and also in the long run prevents waste.

Conservation and environment are nowadays terms which are becoming threadbare through overuse. The Synthetic Rubber business generally has been attacked heftily by the conservationists and the environmentalists. As far as I am aware, this is one disadvantage suffered by synthetic rubber which is not suffered by those producing natural rubber. This aspect places a great strain on the synthetic rubber producer whose existence depends on his ability and expertise in :

- (1) finding cheaper better raw materials
- (2) getting efficient conversions from processes
- (3) improving industrial hygiene of workers
- (4) overcoming landscape and effluent problems
- (5) producing more efficient rubbers

Those of you engaged in natural rubber production should count your blessings — you have one product, from one natural process situated in an environmental Garden of Eden.

It is true to say however that in our modern technological world we cannot really consider an existence without synthetic rubbers. The statistics show that at present and in the foreseeable future there would never be sufficient natural rubber to satisfy the needs of all the world's rubber compounders. The statistics also show that the world uses approximately twice the amount of SR as it does NR.

Fig. 1

Synthetic rubber will hike its share of world market

Thousands of metric tons	World new rubber consumption ^a	
	1976	1986
SYNTHETIC RUBBER	5463	9,004
Styrenebutadiene ^b	3415	5,463
Polybutadiene	739	1,255
Butyl	337	512
Neoprene	272	427
Polyisoprene	253	484
Ethylene-propylene	190	403
Nitrile ^b	159	258
Other synthetic	98	200
NATURAL RUBBER	2702	4,026
TOTAL	8165	13,030
% SYNTHETIC	66.9%	69.1%

a Excludes socialist countries of Eastern Europe and Asia.

b Solid and latex.

Source : International Institute of Synthetic Rubber Producers.

Fig. 2

Growth of total nat. rubber and syn. rubber demand

Trading area	Rate of growth 1960—1970 % p.a.	Total consumption 1975 (x 1000t)	Rate of growth 1975—1980 % p.a.
U.S.A.	4.9	3200	5.3
W. Europe	7.5	2600	5.1
E. Europe	6.2	2300	8.8
Japan	13.0	965	6.6
China	—	335	8.4
Others	8.4	1600	6.8

Fig. 3

World Consumption of Rubber (x 1000 tons)

	NR	SR	Total
1975	3500	7500	11000
1980 (Est)	4500	10500	15000
Growth Rate	5.1%	7.0% p.a.	6.4% p.a.

Even though the extrapolation to 1986 indicates approximately a twofold increase in the amounts of both NR and SR used, the percentage of the latter in the total is still increasing.

If usage does develop as extrapolations indicate, I do not think either side of the rubber industry need worry for their futures.

However, I would like to sound a word of caution, since our industrial development and economic survival might not be so stable. A factor frequently overlooked or inadequately expressed in most statistics given out for the rubber industries is the growth of production in the so called Eastern Bloc countries. In polyisoprene alone, Russia now has an enormous potential capacity and this material is a direct competitor to natural rubber. In almost every country of the Eastern Bloc, and also China there are rapidly increasing large capacities becoming available for all general purpose synthetic rubbers. Is it possible, that these completely controlled economies, with their large independent oil and gas reserves, will be soon in a position to export their rubbers at prices with which we cannot compete. If so, this could indeed be a worry to the natural and synthetic industries outside the Eastern Bloc. An example of what might happen is given by the effect uneconomically low shipping rates, charged by the Russian operators, is having on the Western world's merchant shipping and shipbuilding industry.

Anyway, I am not an economist, only a poor scientist. May I now turn my attention therefore to the technical side of our business and new developments. The technical side brings our two industries NR and SR much closer together.

In its early years the SR industry learned much from the technology of natural rubber as we all know.

I think it is true to say that the SR industry has in more recent years paid back its debt in this respect by giving ideas to the NR industry. Two things in particular stand out :

- (a) the production of high quality and specification controlled NR such as the SMR.
- (b) The oil extension of NR

The first of these was indeed, in my opinion, a significant step forward. The establishment of higher technical specification standards of quality and processability and improved packaging lifted natural rubber out of its dusty Victorian colonial image and placed it on a par with modern technological products. Terms like "ribbed smoke sheet" and "cup-lump" may eventually disappear altogether from the natural rubber man's vocabulary.

The provision of oil extended natural rubber grades is also a necessary development and helps to make NR more competitive with the synthetic polyisoprenes.

If we consider what these two points mean to the user we get one word *CONVENIENCE*. Today everyone is searching for easier and more convenient ways to carry out operations in industry. This should be designed to improve the lot of the worker and to increase his efficiency. At the same time industrial efficiency over all is improved.

It is my belief that the synthetic rubber industry is moving rapidly in this direction and I would like to give a few examples.

Each of these examples could equally well apply to the natural rubber business either now or in the near future.

Oil extended, carbon black masterbatches and ready rubbers

Oil extended SBR's have been available commercially for many years and are very successful. Similarly, limited quantities of carbon black master-batches have been marketed for some time. Today, one of the fastest growing areas in the sales of general purpose synthetic rubbers is that of ready made blends containing oil and black. The combination offers the customer great convenience in that he no longer needs to consume vast amounts of power milling or mixing in these constituents, especially the black. The messy storage, transfer and measuring of loose carbon black is eliminated. This makes the whole operation cleaner and pleasanter for the worker too.

Our company markets such masterbatches of solution polymerised SBR in about 10 grades, arranged according to type and amount of carbon black, oil and rubber. The product under the name Incarb is reaching the 40,000 tons per annum level and is still rising.

The development of the next stage, namely to incorporate sulphur, accelerators and other ingredients to obtain a "ready-rubber" is already well advanced. These developments practically eliminate the need for heavy internal mixers or mills and the products can be directly extruded into treads or other products.

Powdered Rubbers

A logical step past the masterbatch and "ready rubber" stage is to have the mix finely divided into a discreet crumb or powdered form. This would provide greater convenience for pneumatic conveyance and dosing, and greatly facilitate automation, as well as further reducing power consumption.

Considerable progress has been made by a number of companies in this field, though at this time very little is available commercially. Prominent in their publications and patents are such companies as :—

Chemische Werke Huls in Germany
DuPont Company in USA
I. S. R. and Dunlop in U.K.

In producing a viable powdered rubber, it is essential that the material remains free flowing and that it retains this property during storage.

The main problem has been to overcome the inherent and desirable property of tack in the rubber when it is in the powder form without destroying its physical properties and processing characteristics. In published work success is achieved by the addition of materials giving specific surface activity.

The reasons why large scale exploitation has not yet occurred are :

- (a) The cost of preparing the rubber in powdered form exceed the premium which users are at present willing to pay.
- (b) Transportation costs rise because of the relatively low bulk density compared with bales.

Thermoplastic rubbers (TPR's)

Thermoplastic rubbers are now quite well established commercially and several types are available.

Fig. 4

BLOCK

Shell	Kraton	diene, vinyl aromatic
Dupont	Hytrel	polyester
Uniroyal	TRP	polyolefins
Allied Chem.	ET Resins	pe. grafted butyl

RANDOM

ICI	Evatane	ethylene, vinyl acetate
Polymer	Trans pip	trans-polyisoprene

IONIC

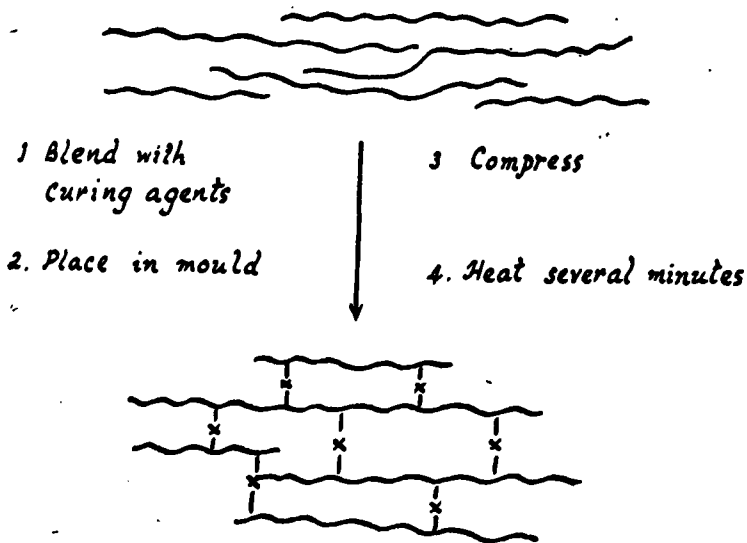
Anchor	Jectothene	polyurethane
DuPont	Surlyn A	ethylene, acrylic acid

It is expected of a TPR that it processes easily, as a thermoplastic material would at elevated temperature and revert to a tough resilient rubber at ambient or working temperatures.

The advantages are obvious. They need no compounding ingredients to produce a permanent chemical vulcanisation and reinforcement. Also because of the reversible nature of their crosslinking, TPR's can be used again and again with no waste.

Fig. 5

Rubber Vulcanisation

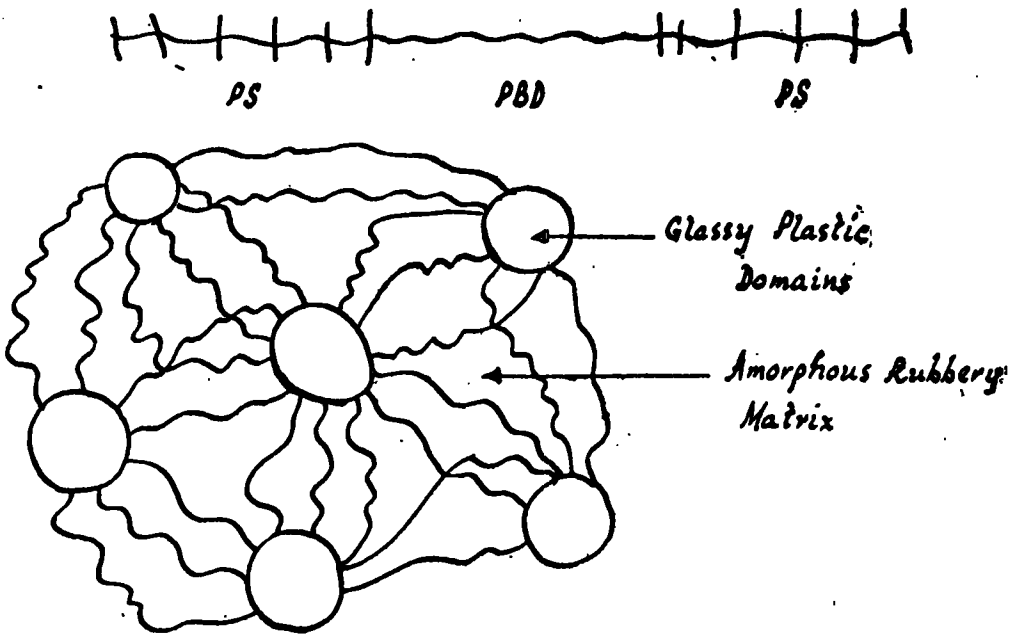


In a TPR cross-linking is achieved instead, usually by a physical means relying on incompatible glassy domains or crystalline domains to provide the internal forces. These discreet domains also provide a linked reinforcing structure analogous to the carbon-black in a conventional vulcanisate.

The first types commercialised were those tri-block copolymers of the ABA type.

Fig. 6

Block - Copolymers



Hydrogenated non-blocky *i.e.* random SBR gives a material with crystalline regions to provide the strength.

Fig. 7

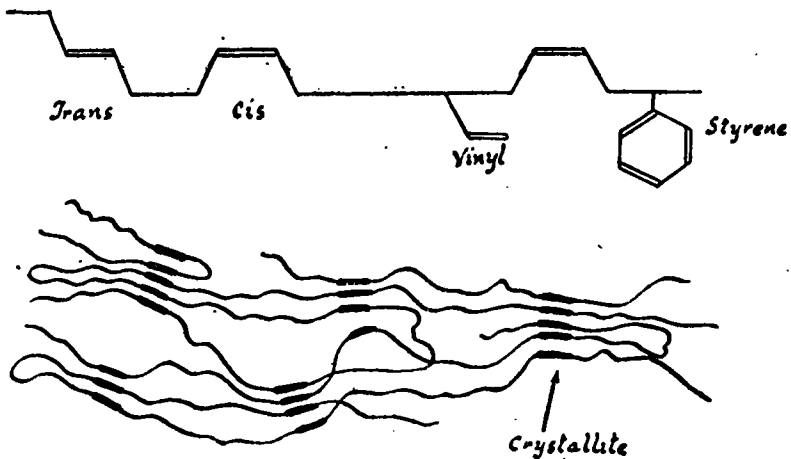


Fig. 8

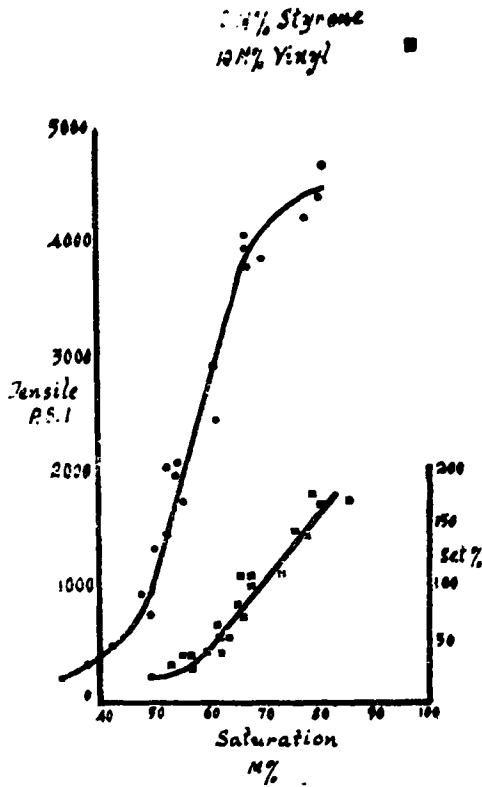
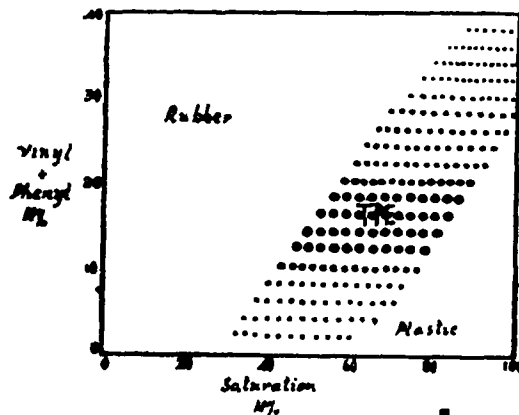


Fig. 9



Analogous to the hydrogenated SBR's are the TPR's based purely on the olefinic monomers ethylene and propylene. These are of more recent introduction into the market, but they are growing very rapidly in use. Particularly in the twilight area between conventional rubbers and ABS plastics or PVC they appear to be ideal. For example, they are favoured in many automobile mouldings, such as radiator grills, dashboards and mudguards, where strength and resilience need to be carefully proportioned.

Fig. 10

Advantages of olefinic thermoplastic rubber

1. Rubber properties without vulcanisation
2. Processable on conventional thermoplastic equipment
3. Wide range of physical properties available
4. Excellent environmental resistance (UV, Ozone)
5. Wide service temperature range (-30 to 150°C)
6. Easily coloured (colour concentrate or painting)
7. Excellent electrical insulating properties
8. Low specific gravity

Fig. 11

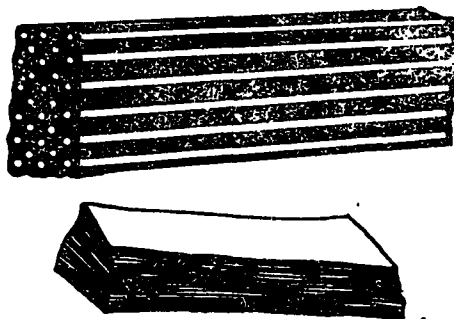
Type	216	225
Specific gravity	0.88	0.88
Hardness, shore A	69	90
Tensile strength, PSI	1000	2000
Elongation at break, %	500	350
100% modulus, PSI	800	2000
Compression set 22 hrs @ RT, %	30	35

Fig. 12

Small rubber goods
 Car components
 Plastic modifiers
 Shoe soling
 Cable insulation
 Hot melt adhesive
 Snowmobile tracks
 Gear wheels, casters
 Orthopaedic supports

An interesting feature for the future of block copolymers which can form domains is that one can now tailor the molecules to give laminar or rod like domains as well as spherical domains.

Fig. 13



So that it is now conceivable to imagine materials capable of forming their own fibres or fabrics *in situ* on cooling. An interesting thought for the future of new rubbers.

Liquid Rubbers

The last of the convenience developments I wish to mention is not really new. These are the liquid rubbers. In fact, "Lorival" a depolymerised natural rubber has been around for years. It is a rather dark viscous liquid of rather limited use and not sold in very large quantities.

The polyurethanes may also be classed as liquid rubbers. Manufacturers of tyres claim from time to time to have made a new revolutionary tyre from liquid rubbers of the polyurethane type. As far as I know none is yet marketed.

I will mention two recent attempts however because they illustrate that casting of liquid rubbers in tyre production seems to be a desirable objective and money is still being spent on such developments.

I quote Rubber Age, March 1970 on a Firestone tyre. "Tests show cast tyres are stronger and more durable than conventional types. Reports indicate they are made of a polymer that needs no carbon black. However, commercial production may be 5 or 10 years away". End of quote.

The second is from European Rubber Journal, April 1976 in an article entitled "Can this be the PU tyre at last?" The description is of a one piece injection moulded tyre called the Polyair LIM (Liquid injection moulded) of an Austrian company. They say that a Ford Escort completed the 1975 Monte Carlo Rally on one set of such tyres.

In addition to the polyurethanes there are the liquid hydrocarbon rubbers. Some are very specialised to produce such things as solid rocket fuels. Others have more general applications.

Fig. 14

Applications of Depolymerised PBD

1. Surface coatings
2. Solid rubber processing aid
3. Primary carpet backing
4. Solid elastomer fabrication

These hydrocarbon chain liquid rubbers are produced by two routes

- (a) by direct polymerisation or
- (b) by depolymerisation of high molecular weight products.

Liquid polybutadienes are typical examples from both processes.

Direct polymerisation allows greater structural control of the liquid polymer, and also the insertion of specific functional end groups if desired, for end to end linking in later processing.

Fig. 15

Basic production methods and properties

- A Polymerisation
 Linear structure
 Narrow molecular weight distribution
 Similar terminal functional groups
- B Depolymerisation
 Branched chains
 Broad molecular weight distribution
 Differing, terminal and pendant functional groups

Fig. 16

Analysis of depolymerised polybutadiene

Viscosity, poise	300
Hydroxyl value	60
Acid value	12
Epoxy content	0.25
Saponification value	15

Casting and ease of processing of liquid rubbers are the main attractions. In addition these polymers find more specific uses in the non-rubber areas such as surface coatings and adhesives.

I would now like to survey briefly the conventional general purpose synthetic rubber field since it is this which has the greatest interface with natural rubber. The general purpose synthetics are hydrocarbon rubbers produced in large quantities, and depending very much on the oil industry for the supply of its monomeric raw materials.

Fig. 17

Current General Purpose Rubbers

Emulsion SBR
 Solution BR'S
 Solution SBR
 Polyisoprene (Natural rubber replacement)
 E P D M

Monomers Needed

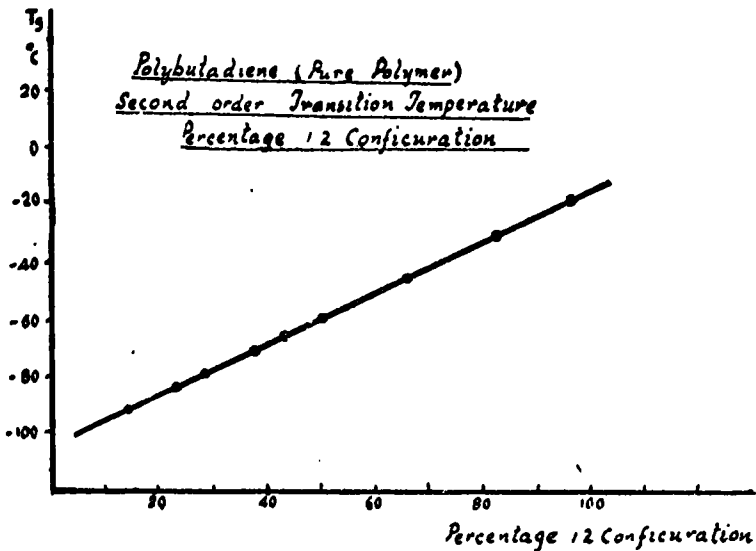
Styrene - butadiene
 Butadiene
 Styrene - butadiene
 Isoprene (isobutene isopentenes)
 Ethylene, propylene (cyclopentadiene,
 dicyclopentadiene, Butadiene),
 1, 4 Hexadiene, Ethylene norbornene.

The styrene-butadiene copolymers are ubiquitous and the random copolymers, the SBR's either emulsion polymerised or solution polymerised are the work horses of the GP synthetic rubbers. They have excellent properties and for passenger car tyres give an ideal balance between wear and road holding safety.

During the politically inspired oil crisis of 1973 - 74, styrene shot up to a ridiculously high price. It became almost impossible to obtain and certainly too costly to use in synthetic rubber.

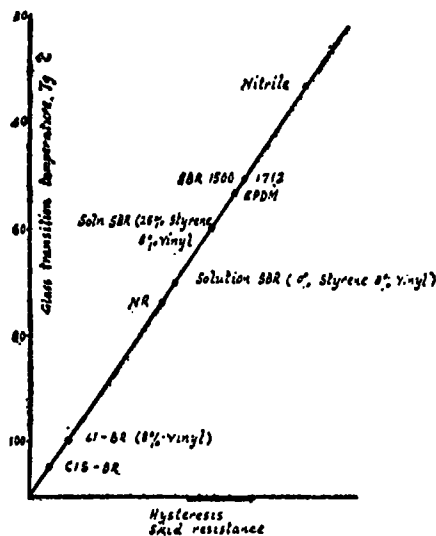
Our company, ISR, was particularly badly affected. We, therefore, re-examined some earlier work which we had done on the relationship between glass transition temperature and the structure in a polybutadiene. It could be shown that the T_g was directly proportional to the vinyl (or 1,2 content) in a homopolymer of butadiene.

Fig. 18



This indicated that a rubber closely similar to that of an SBR could be made from a pure polybutadiene if the vinyl content was adjusted.

Fig. 19



With a vinyl content within the range of 45 — 55% and with the right molecular weight to allow oil extension a polybutadiene could be made which was a very useful substitute for the emulsion polymerised 1712 SBR.

Furthermore, rubbers with specific and advantageous properties could be made by choosing values of vinyl contents above and below this range.

The production of such polybutadienes depends however on having a solution polymerisation plant and on the use of modified butyl lithium catalysts.

Where do we go from here, is there a need for other newer hydrocarbon rubbers? Maybe not! Nevertheless they are already available as far as their technology is concerned, though so far only pilot plant quantities appear to have emerged for evaluation. For example:

Fig. 20

Block homopolymers of butadiene
high 1,2 block high 1,4 block



Radial or coupled homopolymers

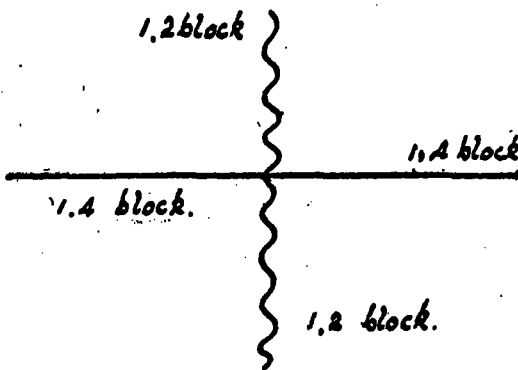
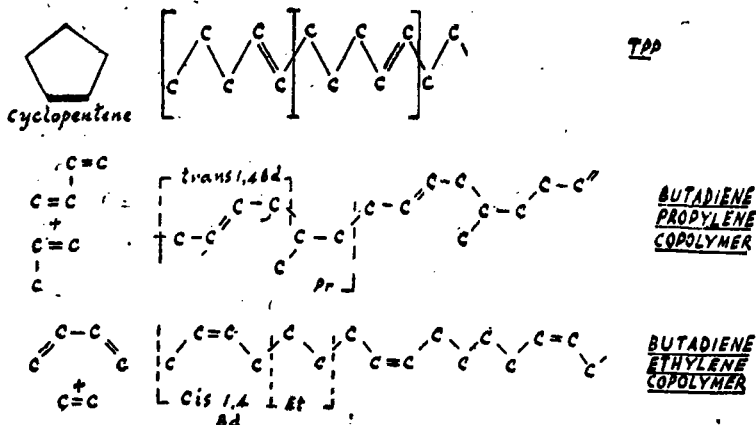


Fig. 21



I hope ladies and gentlemen, that this brief Cook's tour of the rubber industry, has stimulated your thoughts, and to some extent demonstrated once again that NR and SR are very interdependent.