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CONTENTS

I. INTRODUCTION

In the industrial assembly of Romania, the position of the tyre industry is characterized by its dependence on the raw materials which are provided by the chemical and petrochemical industries and by the influence of the automotive industry.

These factors influence not only the volume and range of products but also the technological outlook, which latter follows the general trends of the local situation.

II. TYRE PRODUCTION DYNAMICS

In the period, 197o - 198o, analysed in the present work, the tyre industry is characterized by an important development

Table I

The data presented in Table I illustrate the tyre production dynamics in the present five years plan compared to 197o and the forecast till 198o. It may be observed the accelerated progress of the production and the constancy of the increase rate in both five years periods. The production expressed in weight units, follows approximately the same proportion; production increase during these ten years being predicted for passenger as well as for heavy duty tyres.

The quantitative evolution of the production based on raw materials resources and supported by the investment in new equipment and capacity extensions, is accompanied by a qualitative progress obtained by own research and development efforts as well as by licence acquisition.

Table II

The examination of Table II gives an idea of the range of tyres production in Romania. It reflects in the first place the evolution of internal requirements but at the same time also the availabilities for export which have determined the important increase of passenger tyre production. The truck tyre production does not know important fluctuations as a percentage of the total production, but the absolute quantities are continuously increasing. At the same time the production for agricultural tyres is increasing, though proportionally the increase is somewhat less important.

The decade analyzed in the present work, is characterized by the introduction on a large production scale of a new tyre design, with the meridional disposition of the cord cables in the carcass and with belting with equatorial disposed cables in the breaker.

Table III

As can be seen in the TableIII the year 197o has already marked the orientation towards radial tyres, and in the next ten years this construction will predominate in the passenger tyre range and will start to develop in truck tyres. The option for radial tyres is imposed by the development of the national production of cars, trucks and tractors, by the development of motor vehicle parks simultaneously with the extension of modernised roads. At the same time, this is one of the ways to increase the tyre life by reducing the tread wear and for extending the export availability. In the agricultural tyre range, radial construction will be prefered for the driving wheels in order to ensure a higher traction force, lower fuel consumption and higher productivity in ploughing.

Simultaneously with tyre construction improvement, a permanent need exists for improving the quality of rubber compounds used in bias and radial tyres.

III. THE USE OF NATURAL AND SYNTHETIC RUBBERS IN THE TYRE INDUSTRY

As a consequence of its geographical conditions, Romania is a country which is importing natural rubber; for technical and economical reasons the general trend is towards reducing this import.

Existing oil resources of Romania and the development of the petrochemical industry constitute the complemental factor which determine the continous extension of synthetic rubber use.

For tyre industry, and especially for truck tyres, natural rubber represents the basic elastomer, and its partial replacement in considerable ratio, was possible only recently due to the improvements in solution polymerization of isoprene.

The increase in tyre production volume entails an increasing rubber consumption as illustrated in Fig. 1.

Fig. 1.

For tyre production , synthetic rubber consumption for the period 1965 - 197o is about 5% higher than natural rubber consumption; after 1975 a significant increase in rubber consumption is foreseen in order to maximize production.

The ratio of truck tyres in the present range and the extension of radial construction illustrated in Table II and III calls for the use of significant quantities of natural rubber. A possibility to diminish the natural rubber consumption, for those countries which import it, is to establish their own plants for the production of synthetic polyisoprene, which may replace partially the natural rubber.

At present Romania is planning to construct a plant for high cis-1,4 content polyisoprene; this will significantly modify the consumption of natural and synthetic rubber during the period 1976 - 198o as it can be seen in Fig. 1.

IV. COMPARISON BETWEEN NATURAL RUBBER AND SYNTHETIC cis-1,4 POLYISOPRENE WITH REGARD TO: PROCESSING, PROPERTIES AND TYRE MANUFACTURE.

The experience of the tyre and technical rubber goods industries using synthetic cis-polyisoprene, leads to the conclusion that high cis-1,4 polyisoprene, obtained with the aid of Ziegler - Natta type catalysts, allows the replacement of natural rubber partially or even totaly depending on the manufacture and application of the final products /1, 2, 3/.

In this paper the term of cis-polyisoprene rubber is understood to mean the high cis-1,4 content polymer, in production and application of which Romania is interested

The comparison of natural rubber and cis-polyisoprene characteristics was treated in papers published by both natural rubber producers and synthetic polyisoprene producers /4, 5, 6, 7/. From these works and our own experience we concluded that there are some differences between natural rubber and cis-polyisoprene, with regard to processing and vulcanization characteristics as well as some of vulcanizate properties, differences which are indicated in Table IV.

Table IV

Cis-polyisoprene rubber is in some regards inferior to the natural rubber, but has some superior characteristics, its use in the tyre production shows the following advantages and disadvantages:

Advantages:

- elimination of decrystallization and prior mastication process
- high homogeneity of raw rubber.
- cooler tyre running.
- less shrinkage in extrusion and calendering.
- improved processing safety.

Disadvantages:

- low green strength.
- lower abrasion and tear resistance, especialy at higher temperature.
- higher plasticity of compounds at prolonged processing.

The low qualitative characteristics as well as the disadvantages shown before, limit the use of this rubber for integral replacement of natural rubber in some types of tyres.

Qualitative improvements of cis-polyisoprene based compounds.

In the last years polyisoprene producers and those consumers interested in the use of this rubber, undertook research in order to improve the properties of raw rubber and its compounds, to get closer to the level of natural rubber compounds as much as posible.

Taking into account the differences between synthetic polyisoprene and natural rubber shown in Table IV, the following analysis shows principal ways for improving the properties of compounds based on polyisoprene rubber.

1. Processing characteristics.

Green strength of rubber compounds, is a very important factor during processing especially in radial tyre building.

Polyisoprene rubber producers and consumers are interested in the improvement of this characteristic. Rubber producers acted in he direction of modifying the elastomer by introduction of substances with polar groups in the chains, whose grafting was realized either during the polymerization process /8/ or by mechanical treatment /9/. Though the results obtained are attractive, the process was not yet introduced on industrial scale.

Another way of improving the green strength, is the use of p-nitroso-aniline derivatives and addition of low pressure polyethylene, during the mixing process /10, 11, 12/. Due to its technico-economical advantages, this process found large application in industrial practice.

We prefer to use in our works the p-nitroso-aniline derivatives; the work done with Nitrol (produced by Monsanto) leads to interesting results, as may be seen in Fig. 2.

Fig. 2.

The use of Nitrol produces allow an improvement in green strength and enhancement of some physico-mechanical properties.

Some disadvantages which appear during the processing of compounds based on polyisoprene rubbers are avoided by changing the type of carbon black. For instance good results were obtained when FEF black instead of SRF black was use in compounds for cord rubberizing.

Mechanical break-down, which is more increased in polyisoprene rubber compounds, may be avoided by elimination of the prior mastication process and a proper mixing schedule, reducing the processing time on preheat-mill and feed-up mill. The use of chemical promoters like Nitrol reduces the tendency towards Mooney viscosity lowering.

2. Vulcanization behaviour.

The lack of proteins and fatty acids from synthetic polyisoprene rubber, produces a different vulcanization behaviour in this rubber compared to the natural rubber. This difference is more significant in gum stocks /7, 13/.

By correct choice of the accelerator and of the optimum ratio of accelerator to sulfur, one may obtain similar vulcanization characteristics to those of natural rubber, as may be seen in Fig. 3.

Fig. 3.

Physico-mechanical characteristics platoau and lowering of the reversion tendency may be ensured by optimizing the vulcanization system.

3. Physico-mechanical properties.

Modulus and hardness. At the same level of carbon black, polyisoprene based compounds have lower rigidity than natural rubber compounds. Modulus and hardness of polyisoprene based compounds may reach the same level as those based on natural rubber, by using higher levels of carbon black (an increase of 3 to 5 phr) or higher structure carbon blacks. The increase of carbon black level may adversely influence the elastic properties and heat build-up during service life.

The use of Nitrol allows increase of modulus without an increase of hardness, at the same time increasing elasticity values and lowering the heat-build-up /11/. In this case there is no need of increasing the carbon black level. The use of Nitrol leads to shorter scorch times.

Tear resistance, of polyisoprene rubber compounds is lower than that of natural rubber compounds, and up to the present there is no w known of improving this characteristic.

Low tear resistance values, especially at higher temperature, limit the use of polyisoprene rubber in many applications.

Abrasion resistance. Differences between polyisoprene rubber and natural rubber with regard to abrasion resistance, largely depend on service conditions, being more evident in heavy duty service. An optimum level of abrasion resistance may be obtained by blending polyisoprene rubber with cis-1,4 polybutadiene (aproximately 3o phr); at the same time the use of HAF - HS and ISAF - HS carbon blacks, may lead to an improvement in abrasion resistance.

Blending with polybutadiene rubber leads to an improvement in groove cracking resistance.

Dynamic properties of the polyisoprene rubber are inferior to those of natural rubber, adversely influencing the running potential of the tyres. The use of polybutadiene rubber (25 to 3o phr) for breaker and tread compounds, and p-nitroso-aniline derivatives for carcass and breaker stocks, allows to obtain high performance truck tyres, similar to those made of natural rubber /14/.

We can conclude that there are posibilities of improving polyisoprene rubber characteristics and modifying the compounds, in order to ensure the use of this elastomer in tyre production. However some of the less satisfactory polyisoprene rubber characteristics hinder its use in giant and aeroplane tyres.

V. Trends and achievements in synthetic cis-1,4 polyisoprene use in tyre compounds.

During the last years, in Romania there were done studies with regard to the use of commercial types of high cis-1,4 content polyisoprene rubbers, for bias and radial tyres. The most important results obtained in these studies will be mentioned below.

1. Bias tyres.

The trends of using cis-polyisoprene rubber compared to the present situation are illustrated in Table V.

Table V.

Tread compounds (cape and base)

Cape: Natural rubber is nowdays largely used in tread compounds for truck tyres, being totaly replaced only in passenger and tractor tyres.

The use of cape compounds based only on polyisoprene did not lead to good results due to lower abrasion resistance and groove cracks.

Blending of polyisoprene rubber with 3o to 40% polybutadiene resulted in tyres with similar service life with reference tyres.

For future we can predict for cape compounds, blends like IR/BR; NR/IR/BR; or IR/SBR/BR; the choice depends on truck tyre dimensions and service conditions.

Base. For base of truck tyres NR is minimum 70% used at the same time with lower level of fillers in order to prevent heating during running. The blend NR/IR leads to important technical advantages, and at the same time ensure a good level of physico-mechanical properties and processing characteristics at a 3o - 5o% concentration of natural rubber. It is also possible to add small amounts of BR or SBR, when 35 - 4o phr of HAF black is used.

Breaker and carcass compounds.

Breaker. At present breaker compounds for all types of tyres are made only on a natural rubber base. Technical conditions for the use of polyisoprene rubber in breaker compounds are similar to those analysed for base compounds.

HAF and FEF carbon blacks lead to best result with regard to processing and physico-mechanical characteristics, when high polyisoprene contents are used.

Carcass. Natural rubber alone or in blends with SBR, the latter at levels not exceeding 5o%, is used for carcass compounds.

From our experience we conclude that for this part of the tyre, natural rubber may be tatally replaced, without any difficulties with regard to service aspects.

When polyisoprene is used, FEF carbon black allows a better processing and higher physico-mechanical characteristics, compared to SRF black.

2. Radial tyres.

For radial tyres, we stadied only the passenger and tractor tyres, produced on an industrial scale in Romania. However, some assessments and forecasts may be extended to truck tyres. A forecast in this field is illustrated in Table VI.

Table VI.

Tread compounds (caps).

In the case of radial tyres there are no differenc compared to bias construction with regard to compounds previously analysed.

Sidewall compounds.

For radial tyres this part is subjected to higher dynamic stress and strains compared to bias tyres.

Present sidewall compounds use 3o to 7o parts of natural rubber of the total of elastomers, the rest being either polybutadiene or SBR, depending on tyre type. Experiments done up to how, showed that tha replacement of 5o% of natural rubber with polyisoprene, did not influence the characteristics and performance of the tyres.

From a technological point of view total replacement of natural rubber did not lead to difficulties, running tests are still going on and it is possible that an approximately 1/1 ratio IR/BR blend will ensure satisfactory performance for Romanian road conditions, for sidewalls of passenger and truck tyres.

Breaker belt compounds.

The replacement of natural rubber in breaker compounds on a 5o% level for passenger tyres and 7o% level for tractor tyres produces satisfactory results, and the replacement did not necessitate essential changes in recipes.

cessitate essential changes in recipes.

The use of large amcunte of polyisoprene rubber, especially in passenger tyres, leads to essential changes in recipes and some precautions in processing, due to difficultiee which may appear in cord rubberizing and tyre building.

Further replacement of natural rubber may be possible in principle, but this largely depend on future experiments.

Carcass compounds.

Radial tyre building necessitetes carcass compounds with good green strength. In the case of polyisoprene compounds, this characteristic is not setisfastory. Thus, cable cord rarefaction and relative motions of beads during building and vulcanisation may occur.

For thie reseon the replacement of natural rubber by polyisoprene leade to technologicel difficulties. In carcass formulation for passenger and tractor tyree based on a 5o/5o NR/SBR blend good resulte were obtained when 5o% of the natural rubber wae replaced.

Green strength improvement may be achived by using Nitrol promoter and correct choice of carbon black type and level. This provides the way of extending the use of polyisoprene rubber in carcass compounds, as may be seen in Fig. 4.

Fig. 4.

From the studies and experience achieved untill now, we consider that high cis-1,4 polyisoprene rubber use may be extended to 70% of thenatural rubber level in the case of bias tyres, and 50% minimum for radial tyres.

Present studies attempt to make clear it is possible to extend these ratios.

VI. CONCLUSIONS

Our studies concerning the improvement of tyre compounds and the increase of synthetic rubber consumption were determined both by economical and technological point of views.

Fig. 5.

Among the synthetic rubbers used at present, SBR occupies a predominant position, but it will be considerably influenced in the next years by our own synthetic polyisoprene production, as may be seen from fig. 5.

In our opinion, changes in recipes accompanied by improvements of tyre design will contribute to better road performance, even in case of the growing of synthetic rubber consumption.

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TABLE I

TYRE PRODUCTION DYNAMICS DURING 1970 - 1980

	1970	1975	1980
Relative increase of tyre production, %	100	168	ca.342
Total weight, %	100	180	ca.355

TABLE II

ASSORTMENT OF TYRES DURING 1970 - 1980, %

	1970	1975	1980
Passenger	32	37	46
Truck, bus	47	48	44
Agricultural	21	15	10

TABLE III

DYNAMICS OF THE BIAS AND RADIAL TYRE PRODUCTION
DURING 1970 - 1980

	1970	1975	1980
Passenger			
- bias, %	87	40	30
- radial, %	13	60	70
Truck, bus			
- bias, %	100	92	60
- radial, %	-	8	40
Agricultural			
- bias, %	97	91	85
- radial, %	3	9	15

Table IV

DIFFERENCES BETWEEN THE PROPERTIES OF NATURAL RUBBER AND SYNTHETIC cis-POLYISOPRENE.

Processing characteristic		Vulcanization behaviour		Physico-mechanical properties	
-Green strength	≪	-Cure rate	<	-Modulus	<
-Processing safety	>	-Scorch time	>	-Hardness	<
-Shrinkage in extrusion and calendering	<	-Resistance to reversion	<	-Abrasion resistance	≤
-Tack	<			-Groove cracking resistance	<
-Break-down	>			-Heat build up	<
				-Dynamic properties	<

lower <
higher >
lower or equal ≤
very low ≪

TABLE V

USE OF ELASTOMERS IN BIAS TYRES

I-Present situation II-Forecast

Tyres	Period	Tread: Cape	Tread: Base + Sidewall	Breaker	Carcass
Passenger	I	SBR/BR	SBR/BR	NR	NR/SBR
	II	SBR/BR	SBR/BR	NR/IR	IR/SBR
Medium truck	I	NR/SBR/BR	NR/SBR	NR	NR/SBR
	II	SBR/BR or IR/SBR/BR	NR/IR or NR/IR/BR	NR/IR or NR/IR/BR	IR/SBR
Heavy truck	I	NR or NR/BR	NR or NR/SBR	NR	NR or NR/SBR
	II	NR/IR/BR or IR/BR	NR/IR or NR/IR/BR	NR/IR or NR/IR/BR	IR or IR/SBR
Agricultural	I	SBR	SBR	NR	NR/SBR
	II	SBR	SBR	NR/IR or IR/SBR	IR/SBR

TABLE VI

USE OF ELASTOMERS IN RADIAL TYRES

I-Present situation II-Forecast

Tyres	Period	Tread	Sidewall	Breaker Steel	Breaker Textil	Carcass
Passenger	I	SBR	NR/BR	-	NR	NR/SBR
	II	SBR or SBR/BR	NR/IR/BR or IR/BR	NR/IR	NR/IR	NR/IR/SBR or IR/SBR
Truck	I	-	-	-	-	-
	II	NR/IR/BR or IR/BR	NR/IR/BR or IR/BR	NR/IR	-	NR/IR
Agricultural	I	SBR	NR/SBR	-	NR	NR/SBR
	II	SBR	IR/SBR	-	NR/IR or IR/SBR	NR/IR/SBR or IR/SBR

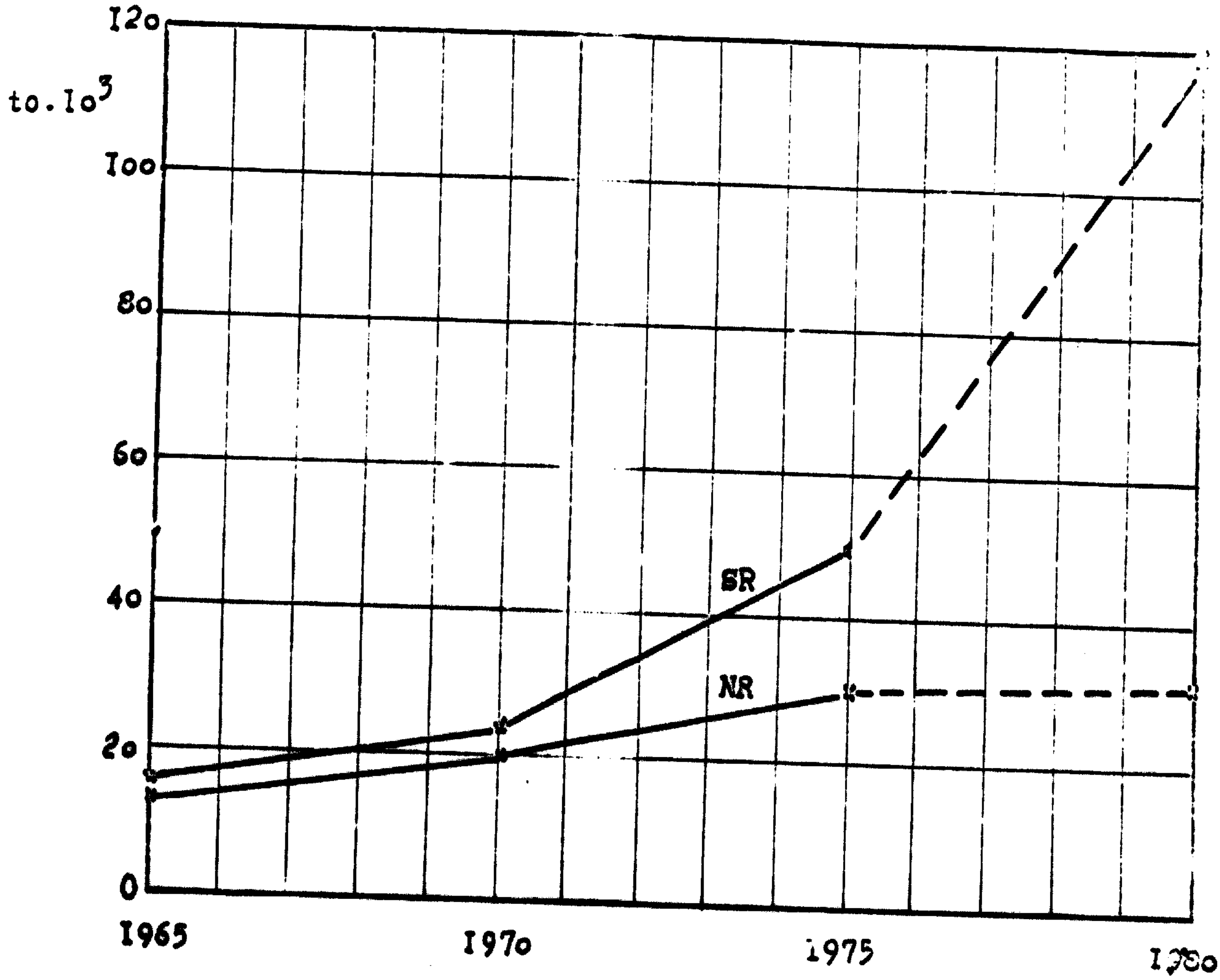


Fig. I. Natural and synthetic rubber consumption.

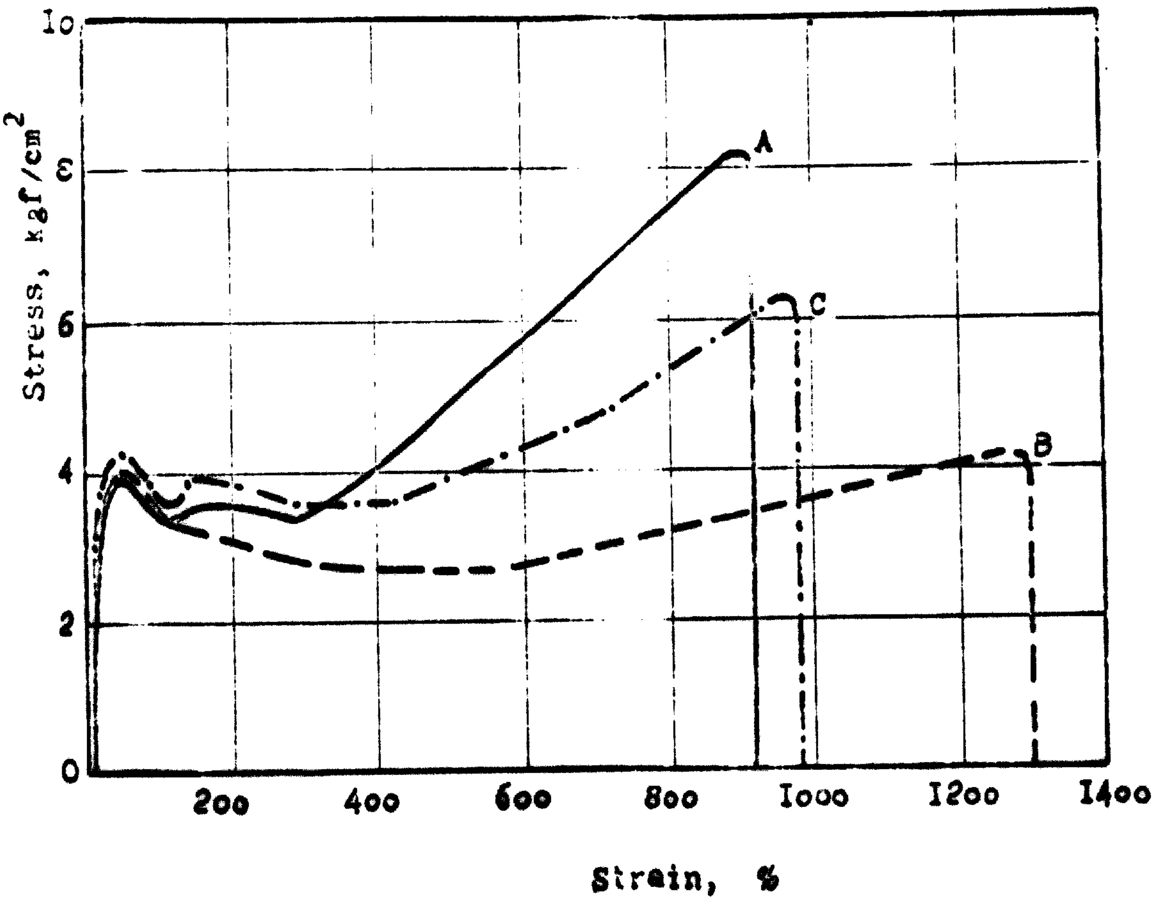


Fig. 2. Green strength of unvulcanized breker compounds.

A – 100 NR

B – 25 NR / 75 high cis IR

C – 25 NR / 75 high cis IR + 0.7 phr Nitrol

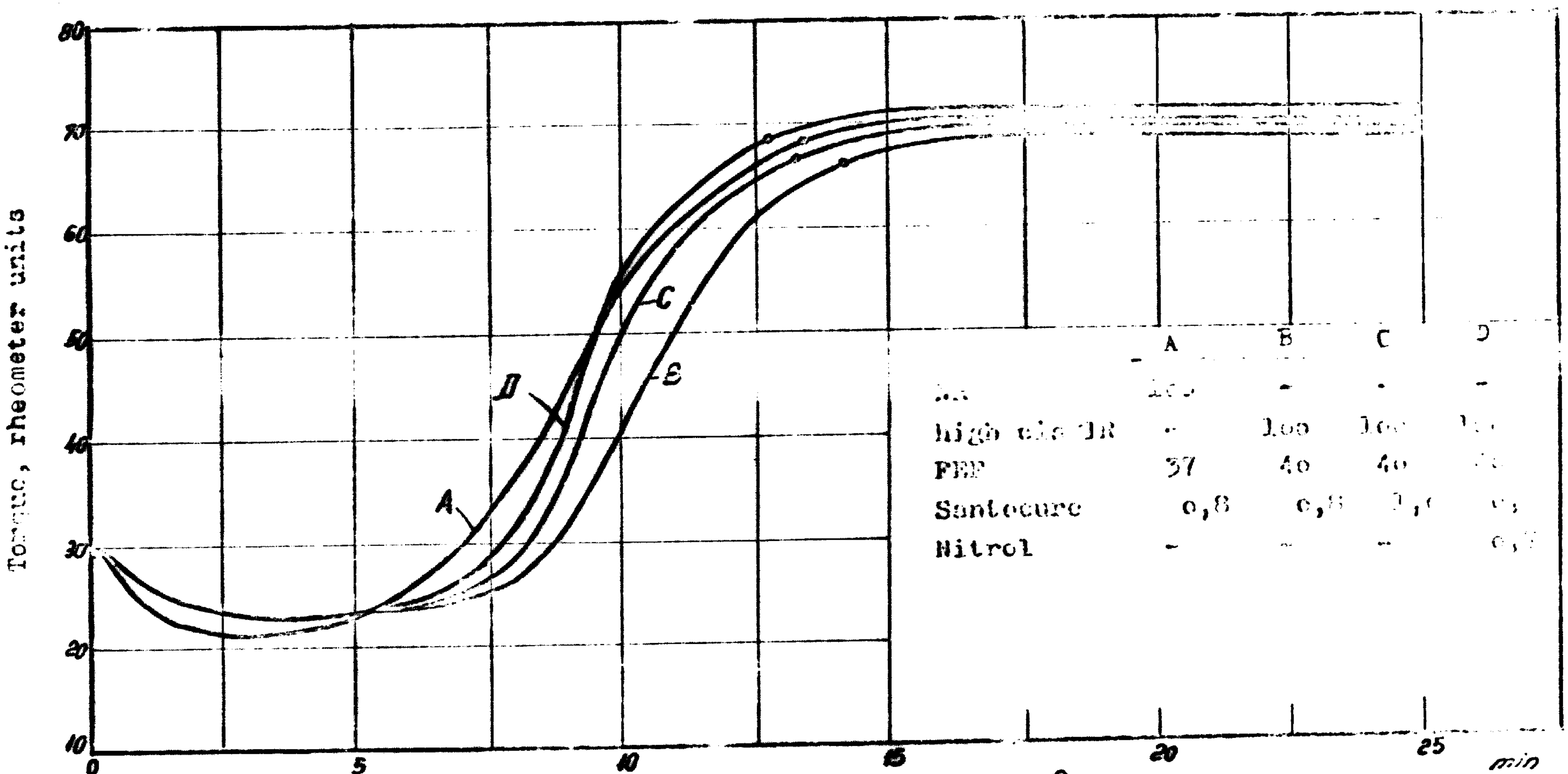
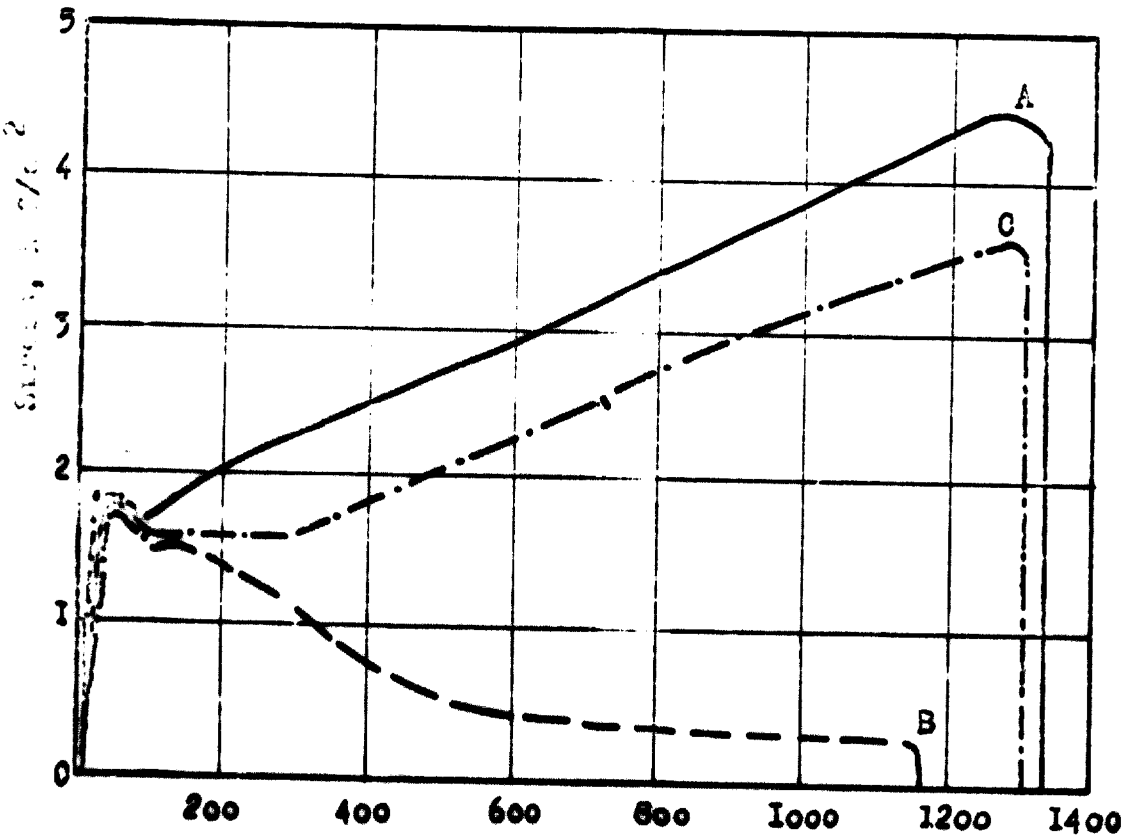


Fig.3. Cure behaviour of breaker compound at 1?0°C



Strain, %

Fig. 4. Green strength of unvulcanized carcass compounds

A - 50 NR / 50 SBR

B - 50 high cis IR / 50 SBR

C - 50 high cis IR / 50 SBR + 0.7 phr Nitrol

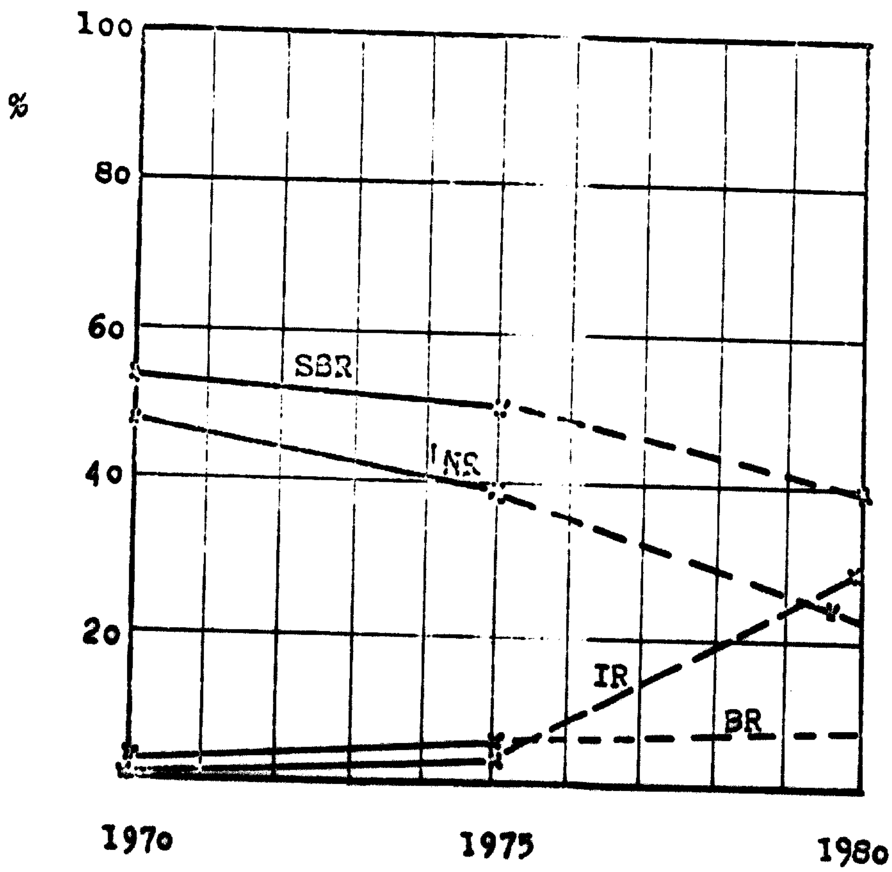


Fig. 5. Contribution of different rubbers to the total rubber consumption.

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