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DEVELOPEMENT OF A NEW TECGNOLOGY FOR PRODUCTION OF BUTYL RECLAIM BY A RADIATION-CHEMICAL METHOD FROM WORN-OUT BUTYL RUBBER BASED PRODUCTS MADE AT CHINESE FACTORIES AND DETERMINATION OF RECLAIM APPLICATIONS

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C O N T E N T S

S U M M A R Y

The report contains a description of the results obtained in the work on determination of the effect of high-energy electrons generated by an electron accelerator ILU-6 on the structure and properties of worn-out bladders/inner tubes stocks based on butyl rubber, made in China.

The effect of the absorbed dose (from 3 to 30 Mrad) on acetone and chloroform extracts, the equilibrium degree of swelling, unsaturation and viscosity of reclaims and physical-mechanical properties of their vulcanizates, also data on the effect of adding 10 p.h.r. bladder and inner tube reclaims obtained at the absorbed doses of 5,7 and 10 Mrad on the properties of bladder and inner tube rubbers made in the USSR are reported.

There is a description of the technology for producing an experimental-industrial lot of radiation butyl reclaim (1.5 tons) from Chinese bladders, and also the results of its testing in the Chinese Republic in a bladder compound.

The tests have shown the possibility of replacing up to 20 p.h.r. butyl rubber in the Chinese bladder stocks by the radiation butyl reclaim obtained at the absorbed dose of 6 Mrad.

Data on the composition of gaseous products of bladder stocks radiolysis, obtained by the method of gas-absorption chromatography, on trying out the procedure for dosimetry and measurement of the absorbed energy distribution of fast electrons in rubber crumb is presented.

Technical and economic grounds for the expediency of installing an experimental-industrial (pilot) plant (with the annual capacity of 1,300 tons) to produce radiation butyl reclaim from bladders in the Chinese Republic are given.

I N T R O D U C T I O N

In accordance with Contract No.89/190/SM signed in 1989 by UNIDO and TRI (the Tyre Research Institute), TRI with participation of a contractor - the Institute of Physical Chemistry (IPhCh) attached to the Ukrainian Academy of Science-was to develop a technology for producing butyl reclaim by a radiation method with the use of an electron accelerator ILU-6 from worn-out bladders and inner tubes manufactured in China, and also to give out a principle description of a pilot plant for producing butyl reclaim by a radiation method from Chinese bladders with a list of the general technological parameters of the process, the processing equipment, energy consumption, etc.

In the course of carrying out the contractual work TRI transfered 4 reports to UNIDO and the Chinese counterpart:

- Principle technology of manufacture and estimated technical/ /economic characteristics of application of reclaim from rezin-cured butyl rubber compounds by a radiation method.

  This information was based on the results of the work that had been done in the Soviet Union earlier for producing butyl reclaim by the radiation method from bladders made in the USSR.
- Study of the effect of high-energy electrons on the structure and properties of butyl rubber compounds of worn-out bladders and inner tubes produced in China.
- A pilot plant for production of butyl reclaim by the radiation method from bladders made in China.
- The Draft Final Report "Development of a new technology for production of butyl reclaim by a radiation-chemical method from worn-out butyl rubber based products made at Chinese factories and determination of reclaim applications".

The present report finished off with the account for UNIDO comments on the Draft Final Report, is the Final Report on Contract 89/190/SM.

1. EFFECT OF HIGH-ENERGY ELECTRONS ON THE STRUCTURE AND PROPERTIES OF WORN-OUT BUTYL RUBBER BLADDERS AND INNER TUBES PRODUCED IN THE PEOPLE'S REPUBLIC OF CHINA.

1.1 Preparation of initial raw materials

1.1.1 Characteristics of initial raw materials

Initial raw materials for this work were worn-out bladders and inner tubes supplied from the Chinese Republic.

To study the effect of the irradiation conditions on the quality of the obtained reclaim and to produce experimental samples of reclaim for their subsequent testing in China, there were received from China 170kg bladders cut into 2 or 4 parts and 25 kg of whole inner tubes.

For production of an experimental-industrial lot that was to be tested in China, 7 tons of worn-out bladders were shipped by railway from the Chinese Republic. Since these bladders travelled over 6 months and the work was to be done in due time, the Chinese party sent 2t. bladders by air at TRI request.

An experimental-industrial lot of reclaim was made from these bladders and sent to China for the industrial trial in rubber compounds.

Further below there is data on the formulation and properties of these materials (according to the Chinese data).

Bladders.

Bladder compound composition(p.h.r.)

Butyl rubber with 1.6% unsaturation
(Polysar rubber PB 301).....100

Chlorinated butyl rubber.....5
Resin 2402(Resin 101 B) 12
Carbon black HAF .....50 to 60
Mineral oil or petroleum jelly 5
Zinc oxide .....5 to 10

Curing cycle: 2.0 to 3.5 h
170 to 180°C

Vulcanizate properties:

Hardness, arbitrary units .....58 to 68
Tensile strength, MPa .....11 to 14
Relative elongation, % .....550 to 660
Tension set, % .....20 to 30

Inner tubes

Inner tube compound composition(p.h.r.)

Butyl rubber 100
Sulfur .....1.7 to 2.0
Stearic acid 1.0
Carbon black FEF .....25 to 30

Carbon black SRF .....25 to 30
Rubber processing oil .....15 to 20
TMTD 1.0
Altax (MBTS) 0.5
Captax (MBT) 0.5
Zinc oxide 5.0

Vulcanizate properties:
Tensile strength,MPa 9.0
Relative elongation,% 500
Tension set,% 35

To obtain sulfur vulcanizates from the break-down products of the bladders and inner tubes we have taken the ingredients used in China,i.e.sulfur,Captax,TMTD,zinc oxide.The bladder reclaim curing has also been done with n-octylphenolformaldehyde resin SP-1045 used in the USSR for curing of bladders.

1.1.2 Production of rubber crumb from bladders and inner tubes.

In the case of the accelerator with the electron energy of 2 MeV the size of the particles of the rubber crumb can be 5 mm.

Due to the small amount of the initial materials received from China their grinding was done in a high-speed rotor grinder of a cutting type with the following technical characteristics:

Rotor diameter at cutting edges,mm..... 400±10
Cutting edge length,mm ..... 85 to 90
Shell knife length,mm ..... 85 to 90
Plug knife length,mm.....85 to 90
Linear cutting speed .....12 to 15
Number of plug knives.....5
Number of shell knives.....4
Electric motor power,kwt.....15
Overall dimensions,mm.....1075X840X1010
Weight,kg(without pneumatic transportation system) .....up to 900

2 t of bladders were first crushed in the coarse crushing machine. Grinding of the resulting 150X150mm rubber pieces to rubber crumb with the particle size under 7mm was done on the grinding mills

with ribbed rolls,using a 0.2% water solution of surfactants to prevent agglomeration of the rubber. Having passed through the mills the partially ground rubber was fed by an elevator to a one-tier vibratory sieve. The tailings from the sieve went back to the nip of the rolls. Due to the absence of a suitable pneumatic drier the sieve fraction containing up to 15% moisture dried in the open air till the residual moisture content became 1% maximum.

The output of the mills was 360-400 kg/h; the surfactant consumption was 0.6 kg per 1 t. rubber crumb.

Further below there are characteriatics of the equipment used.

Coarse crushing machine for bladders

Dimensions of the charging opening:	1260X400 mm
Overall dimensions:	3000X2200X3000 mm
Electric motor power:	134 kwt
Output:	3 t/h

Grinding mills

Roll length:	800 mm
Roll diameter:	550 mm
friction:	1:3.08
Electric motor power:	160 kwt

Vibratory sieve for sieving rubber crumb

Slope angle:	4°30'
Number of double vibrations:	265/min
Overall dimensions:	3110X1412X870 mm
Electric motor power:	1.7 kwt

1.2 Irradiation of bladder/inner tube rubber stocks by high-energy electrons

The rubber crumb from bladders and inner tubes was exposed to the action of accelerated electrons generated by the electron accelerator ILU-6 at the following absorbed doses:
bladders - 3,5,7,10,12,15,20,30 Mrad
inner tubes-5,7,10,12,15,20 Mrad

1.2.1. Electron accelerator ILU-6

A pulse linear accelerator ILU-6 model 6 designed by the Institute of Nuclear Physics (the Siberian Division of the USSR Academy of Sciences, the city of Novosibirsk) was used as a source of radiation. This electrophysical apparatus is designed for the operation as a source of ionizing radiaton as part of radiation plants of

different applications under the following conditions:

—ambient air temperature: from +10°C to+35°C

—relative humidity :up to 98% at the temperature of the ambient air + 25°C

General parameters and dimensions of the electron accelerator ILU-6

1. Parameters of the accelerated electron beam:
   a) energy,MeV.... range1: 0.5....1.0
      range2: 1.0....1.5
      range3: 1.5....2.0
   b) energy variations in the beam,%...10 maximum
   c) energy instability, % .....10 maximum
   d) limits of the mean current adjustment,mA:
      range1: 0.....40
      range2: 0.....20
      range3: 0.....13.5
   e) instability of the mean current during an hour of the accelerator operation with maximum energy and power,%
      —7 maximum
   f) maximum current in a pulse,A...up to 1
   g) maximum power within the whole range of energies,kwt..... 20 minimum
2. Frequency of the accelerating voltage,MHz....120-127.
3. Duration of the current pulse, μs:
      range1 - up to 700
      range2 - up to 600
      range3 - up to 500
4. Frequency of pulse repetition:
      range1.....2...300
      range2 and 3...2... 50
5. Power of the emergent beam from the total power is for rectilinear scan at the non-uniformity of the linear current density better than ± 10% on the length of 800 mm,%.....80 minimum.
6. Dimensions of the outlet window,mm.....980×75
7. Overall dimensions
   —diameter of the tank with flanges-1230 mm
   —dimension with protruding parts -2300 mm
   —overall hight with a funnel -3100 mm
   —height of the tank proper -1125 mm
   —tank hight with entry and pumps -1800 mm

8. Accelerator weight...2200kg,control cabinet...850kg,power supply cabinet 1...1010 kg
power supply cabinet 2...1300kg,
power supply cabinet 3...1050 kg.
Power units for pumps(PU)...72kg,
for roughing-down pump AVR-50...200kg.

9. Time of going into the mode of operation,maximum:
-after a stop of less than an hour ..... 10 min.
-after a stop of 48 hours maximum-120 min.
-after spontaneons de-energezing-5 mim.

10. Parameters of the power supply line:
-voltage -380/220V
-number of phases -3
-frequency -50 Herz

11. Power requirement,kwt - 120 maximum

12. Connection of the plant to the power supply line should be from a separate transformer with the overall power of 180 kVA minimum, via a device providing for a visible break in the power supply circuit at a complete removal of voltage.

13. The plant should have a separate grounding loop.

14. Cooling of the accelerator proper and the power supply system(cabinets 2,3,4)with distilled water of the following parameters:
-resistivity.....minimum 10^2 Ohm°m
-pressure at the inlet of the system.....minimum 322kPa(4atm.)
but maximum 588kPa(6atm.)
-pressure at the outlet of the system.....max.98kPa(1atm)
-temperature at the inlet of the system.....max.24°C,
min.the dew point in the accelerator room
-flow rate for the accelerator .....min.3.6m^3/h

-flow rate for the
power supply system.....0.9m^3/h

15. Cooling of the outlet window foil.....by compressed air free of dust and traces of oil with the following parameters:
-pressure at the inlet of the system.....min.294kPa(3atm.)
-air flow rate.....min.200m^3/h
under normal conditions

16. Average time of failure-free performance at nominal parameters including maintenance should be minimum 1000 hours,maintenance taking maximum 25% of this time.

17. Normal operating period of the plant is 10 years except for the accelerator units whose life is defined in the specifications

for these parts. When the normal operating time expires the plant is to be rechecked in terms of all technical requirements. In case of its compliance to the specfications it can be used further on

1.3. Methodology

Viscosity measurement

Samples for measurement of Mooney viscosity were prepared on the mills $320\frac{160}{160}$, passing the weighed amount of reclaim 10 times by 300g through the 2mm nip between the rolls. Mooney viscosity was determined according to GOST 10722-76.

Reclaim curing and determination of physical-mechanical properties

Compounds for reclaim curing and subsequent determination of its physical-mechanical properties were prepared by the formulations and under the conditions given in Table 1.

Table 1.

Formulation of reclaim compounds and their curing conditions

Type of curing	Ingredients		Sequence of ingredient introduction., min.	Curing conditions	
	name	p.h.r.		°C	time, min.
resin(I)	reclaim	100	0	165	50
	SP-1045 (n-octylphenol-formaldehyde resin)	10	4 end of mixing 10		
resin(II)	reclaim SP-1045	100 15	id.	id.	id.
sulphur (I)	reclaim	100	0	id.	id.
	zinc oxide	2.5	2		
	thiuram	0.5	4		
	captax	0.25	4		
	sulphur	1.0	5 end of mixing 7		
sulphur (II)	reclaim zinc oxide	100 5	id.	id.	id.

thiuram captax sulphur	1 0.5 2			1c.

Reclaim from bladders was cured with resin and sulphur, reclaim from inner tubes only with sulphur.

Physical-mechanical properties of vulcanizates (tensile strength, relative elongation) were determined according to GOST 270-75, and tear resistance according to GOST 262-79.

Acetone and chloroform extracts of the radiation reclaim (in some cases those of their vulcanizates as well) and their equilibrium degree of swelling in m-xylol were determined too. The equilibrium degree of swelling and chloroform extract (sol fraction) were used to judge about a degree of the radiation products breakdown.

Extract determination

To measure the extracts the weighed amounts of the reclaim or the vulcanizate (cut into small pieces) were placed into a fabric bag and extracted by hot acetone in the Soxhlet apparatus during 24 hours. Then by warming it up in the thermostat at 60°C the bag with the extracted material was brought to a constant weight.

After the acetone extraction we did chloroform extraction in a similar way. The value of the acetone and chloroform extracts (in %) was found as a relation of the corresponding reduction of the weighed mass to the initial weighed amount and to the weighed mass after the acetone extraction respectively.

Determination of the equilibrium degree of swelling.

To determine the equilibrium degree of swelling a punched basket from aluminium foil with the reclaim weighed mass of about 0.1g (cut into small pieces) was placed in m-xylol for 24 hours; then the excess of the solvent was removed from the weighed amount by centrifugation during 6 to 8 min. The baskets were weighed after the centrifugation and after bringing them to a constant mass. The equilibrium degree of swelling (in %) was calculated as a relation of the swollen weighed mass to the mass of weighed amount after bringing it to the constant mass.

The equilibrium degree of swelling of the reclaim vulcanizates was determined in other ways. A piece of the vulcanizate about 5X5mm was placed in m-xylol for 24 hours; then, after removing the solvent from its surface with filter paper, the sample was weighed. The calculation of the equilibrium degree of swelling was made as in the first case.

Determination of unsaturation.

Unsaturation was determined by the method of ozonolysis on the ADC-3 machine (a double bond analyzer) for the sol fraction of the bladder compound after its radiation processing by the absorbed doses from 7 to 30 Mrad and for the sol fraction of the unirradiated butyl

rubber БК-1675 T produced in the USSR.

The principle of this machine operation consists in the following.

An oxygen flow is passed through the ozonator where part of it is converted into ozone. Then the blend of the gases passes through a flow reactor where the sample is injected.

After the reactor the flow comes into a gas cell where the ozone amount is recorded with the use of U7 radiation and is emitted into the atmosphere.

The ozone amount absorbed by the substance placed into the reactor is registered by the recorder as an absorbtion curve which is immediately integrated with the aid of a special integrator.

The reactor was placed into a Dewar flask cooled with a special device by liquid nitrogen.

The temperature around the reactor was maintained at about 200--210°K. In this case the volatilization of the chloroform and its ingress into the gas cell was eliminated and the reaction of ozonolysis ocurred rapidly enough.

The sample was injected into the reactor with a 1 ml medical syringe via a rubber membrane.

Before the analysis the instrument was calibrated with stilbene solution of five different concentrations in chloroform.

The solution of each concentration of both stilbene and chloroform extract was analyzed at least 4 times.

In the course of the analysis of the chloroform extracts there were some distortions of the absorption curves. This can be explained either by slower interaction of spatially hampered double bonds with ozone or, which is more likely, by the ozone interaction with the resin components used for curing of bladder compounds.

The control check showed that some of the substituted phenols interact quantitatively with ozone under the conditions of the analysis.

In connection with this it doesn't seem possible to assess an error made in the data on the number of the double bonds in the sol fraction due the interaction of the resin components with the ozone.

Application of the dosimetry procedure and determination of the distribution of energy absorbed by fast electrons in the rubber crumb.

We have studied the effect of the energetic(the energy of electrons, the average current of the electron beam, the absorbed dose during one pass)and technological(rubber compound transportation conditions in the irradiation zone)parameters of irradiation to determine the size of the absorbing zone and its distribution in the rubber crumb. The investigation was done at the absorbed dose from 2 to 30 Mrad.

The dosimetry was carried out on the electron accelerator ILU-6 according to the measurement procedure with the aid of film badges (chemical dosimeters)ДПЦ-2/25 and СОПД(Ф)-5/150 (Table 2)

Table 2.

Characteristics of dosimetric films used for dosimetry

Characteristics of dosimeters	ДПЦ - 2/25	СОПД (Ф) - 5/I50
1. Radiation type	accelerated electrons, photons	accelerated electrons, photons
2. Range of absorbed doses	2 - 25 Mrad	0,5 - 15 Mrad
3. Length of the maximum absorption wave	515 nm	525 nm
4. Thickness	$30 \cdot 10^{-6}$m	$70 \cdot 10^{-6}$m
5. Error limit	±12%	±15%
6. Temperature during irradiation	20+80°C	15+50

ДПЦ-2/25 dosimeter. The measurement of the optical density variation was done on the spectrophotometer"Spekord UV-ViS" at the maximum

absorption wave length of 515 mm. The absorbed dose was determined by the calibration chart of the optical density variation dependence on the absorbed dose.

ДПЩ -2/25 dosimeter was calibrated on the ^{60}Co γ -unit УК-250000 certified by the VNII of physico-Technical and Radiotechnical Measurements with the reference chemical detectors ДОТ-25/200 in accordance with GOST 20268-83. The relative error in the absorbed dose measurements at the confidence level of 0,95 for ДПЩ-2/25 was 10 %.

The working temperature range of the irradiation was 10-60°C.

СОПД(Ф-5/150) dosimeter (a standard reference of the absorbed dose of the photon and electron irradiation)

The measurements were taken on the СФ-26 spectrophotometer with the wave length of λ=512mm relative to the reference specimen.

The absorbed dose was determined by the dependence (a calibration characteristic curve) of the absorbed dose on the optical density given in the certificate for the standard specimen.

The relative limit error of the absorbed dose measurement with the aid of the standard specimen is 15% at the confidence level of 0.95.

The range of the working temperatures of the irradiation is 15-50°C.

To eliminate the by-action of the gas emission products during the radiolysis of the butyl rubber compounds the chemical dosimeters were packed in lavsan film.

We have also run comparative testing for irradiation of СОПД (Ф)-5/150 and ДПЩ-2/25 dosimeters on the ^{60}Co γ-unit УК-250 000.

The irradiation of the dosimetric films was done at the rate of the absorbed dose of 743 rad/s and at the absorbed doses of 2.5 and 5 Mrad.

The dose in the ДПЩ-2/25 films practically corresponded to 2.5 and 5 Mrad whereas the dose in СОПД(Ф)-5/150 had a scatter up to the limit measurement error.

The irradiation of film badges ДПЩ-2/25 and СОПД(Ф)-5/150 on the electron accelerator ILU-6 was done under the following conditions:

accelerated electrons energy.....2.0 MeV
beam current.....4.0 mA
conveyor speed.....11 mm/s
number of passes.....6-12

The comparative results showed that the scatter of the values obtained on differfnt films was within the relative error limits admissible for them.

Both types of the dosimetric films under different operating conditions of the accelerator ILU-6 were used to measure the absorbed dose at the surface and in the thickness of the rubber crumb layer to 10 mm.The crumb was on a metal tray.

The difference in the absorbed dose between the top and the bottom of the radiated crumb with the particle size of 3 to 5 mm was:

∓ 20 % for bladder compounds

± 10 % for inner tube compounds

An increase in the geometrical dimensions of the crumb particles increases significantly a measurement error of the dosimetry method applied.Thus,as a result of this work a dosimetry procedure has been developed to provide control over the absorbed energy of the fast electrons at the selected thickness of the bulk crumb layer.

1.4. Effect of the absorbed dose on the structure and properties of the radiation breakdown products cf butyl bladders and inner tubes.

The irradiation conditions:

energy of electrons .....2 MeV
electron beam current .....10 mA
thickness of irradiated crumb layer.....10 mm
distance from inlet window foil to material..100 mm
conveyor speed .....2.5 to 4.7 cm/s

1.4.1. Radiation butyl reclaim behavior during mechanical processing

Visual assessment of the irradiated material

The product of the bladder crumb irradiation is :

at 3 Mrad ..... the irradiated crumb doesn't practically differ from the original crumb

5,7 Mrad..... the irradiated crumb is softer to the touch then the original crumb but it almost doesn't clot

10,12,15Mrad.. the irradiated crumb sticks together

20,30 Mrad... the irradiated crumb becomes all sticky mass

The product of the inner tube irradiation is:

5 Mrad..... the irradiated crumb is soft but not sticky
10 Mrad..... the irradiated crumb sticks together
15,20 Mrad... the irradiated crumb is all sticky mass.

We determined the equilibrium degree of swelling, the acetone and chloroform extracts of the reclaim samples and their vulcanizates, the physical/mechanical properties of the reclaim vulcenizates and also the plasto-elastic properties and unsaturation of the reclaim.

Before the measurement of the reclaim properties we carried out its homogenisation on the mills 320 $\frac{160}{160}$. For this purpose the weighed amount of the reclaim(300 g) was passed 20 times through the 1 mm nip between the rolls.

The reclaim behavior during this processing on the mills and its appearance after the milling are reported in Table 3.

Table 3

RADIATION RECLAIM BEHAVIOR DURING MILLING

Initial material	Absorbed dose, Mrad	Number of passes after which the reclaim fabric sheets well	Appearance of the reclaim after milling
Bladder	3	reclaim is not milled well	very rough stiff sheet
	5	12	uneven, not smooth sheet
	7	3	rugged sheet, not smooth
	8	immediately	id.
	9	id.	smooth sheet
	*) 10	id.	smooth, sticky sheet
	*) 12	id.	very sticky sheet
	15	sticks to the roll at once, it cannot be incised with a knife	impossible to remove from the roll as skin
	20	id.	id.
	30	id.	id.

Table 2 continued

Inner tube	5	15	uneven, (rugged) .
	7	9	id.
	10	at once	soft sheet
	12	id.	soft and sticky sheet
	15	sticks and flows over the roll	impossible to process, goes under the cheek plates
	20	id.	id.

*) Due to its stickiness the reclaim obtained at the absorbed doses of 10 and 12 Mrad was passed through the nip 12 and 8 times, respectively.

1.4.2. Dependence of the properties of bladder/inner tube breakdown products on the value of the absorbed dose.

Since an exact determination of double bonds in the irradiated worn-out butyl rubber is difficult not only by the method of ozonization but also by other methods of estimating double bonds in such systems, we have studied the concentration on unsaturated C=C-bonds in pure rubbers used for bladder production in the Chinese Republic.

Table 4 shows content of double bonds in butyl rubbers of 2 different grades at different absorbed doses.

Table 4

Butyl rubber unsaturation (%) at different doses (Mrad.)

Rubber	Dose, Mrad						
	0	5	8	10	13	15	20
Polysar 301	1.97	2.60	3.30	3.41	3.50	3.70	3.76
JSR - 268	1.91	2.20	3.20	3.40	3.24	3.47	3.97

A relative error of measuring unsaturation did not exceed 10% and in a majority of cases it was 4-5%. As it follows from Table 4 butyl rubber unsaturation grows twice as much in the interval from 0 to 20Mrad. One should expect that after the radiation of worn-out rubber stocks there will be a similar increase of double bond quantity in the carbon component of rubber stocks.

Indeed, one can see from Table 5 that unsaturation grows in irradi-

ation of both bladder and inner tube stocks.

Table 5

Unsaturation in butyl-based rubber stocks,%

Dose, Mrad	Bladder stock	Inner tube stock
3	0,25	
5	0,64	
7		0,46
10		0,76
12	0,74	
15		0,92

With the growth of the absorbed dose the content of the chloroform extract (sol fraction) in the radiation breakdown products of both bladders and inner tubes increases (Fig.1). In the case of bladders the limit values of the sol fraction are reached practically at 30 Mrad with over 90% of the rubber substance turning into a soluble state.

The equilibrium degree of the bladder breakdown products swelling varies as a curve with the maximum (Fig.2a). However, if we calculate the degree of swelling in respect to the rubber substance content in the weighed amount after removing the solvent, then one can see that the degree of swelling grows up to about 2000% with the growth of the absorbed dose (Fig.2a.,curve 2).

The data in Figs.1 and 2b also evidences about a high degree of the inner tube radiation breakdown, though it is slightly lower than in the case of the bladders. For example, the equilibrium degree of swelling about 1000% is achieved in the bladder case at the absorbed dose of 7 Mrad, and in the inner tube case it occurs at 12 Mrad. The sol fraction of the breakdown products is about 30% for either type of rubber. The differences in the degrees of the radiation breakdown of bladders and inner tubes can be partially explained by greater density of the vulcanization network in the original inner tube rubber.

Table 6 shows the properties of the reclaim obtained from bladders and inner tubes and the properties of its vulcanizates.

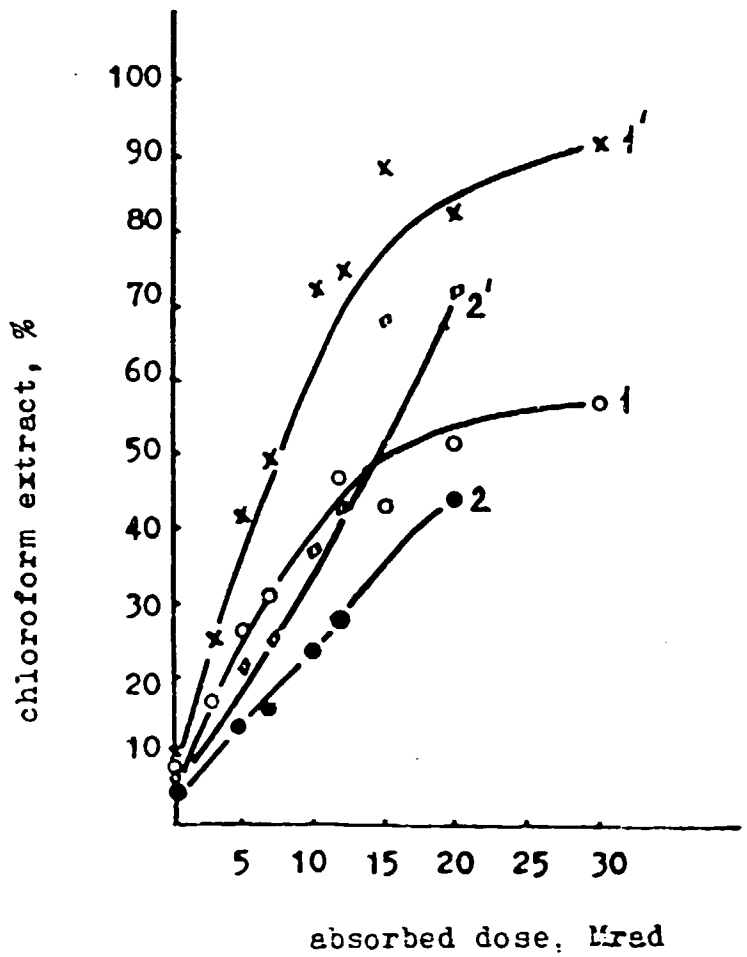


Fig.1. Content of the chloroform extract in the radiation breakdown products of bladders(1, 1')and inner tubes(2,2') as a function of the absorbed dose;

1,2-with respect to the weight of the specimen after the removal of the solvent;

1',2'-with respect to the content of the rubber substance remaining in the specimen after the removal of the solvent.

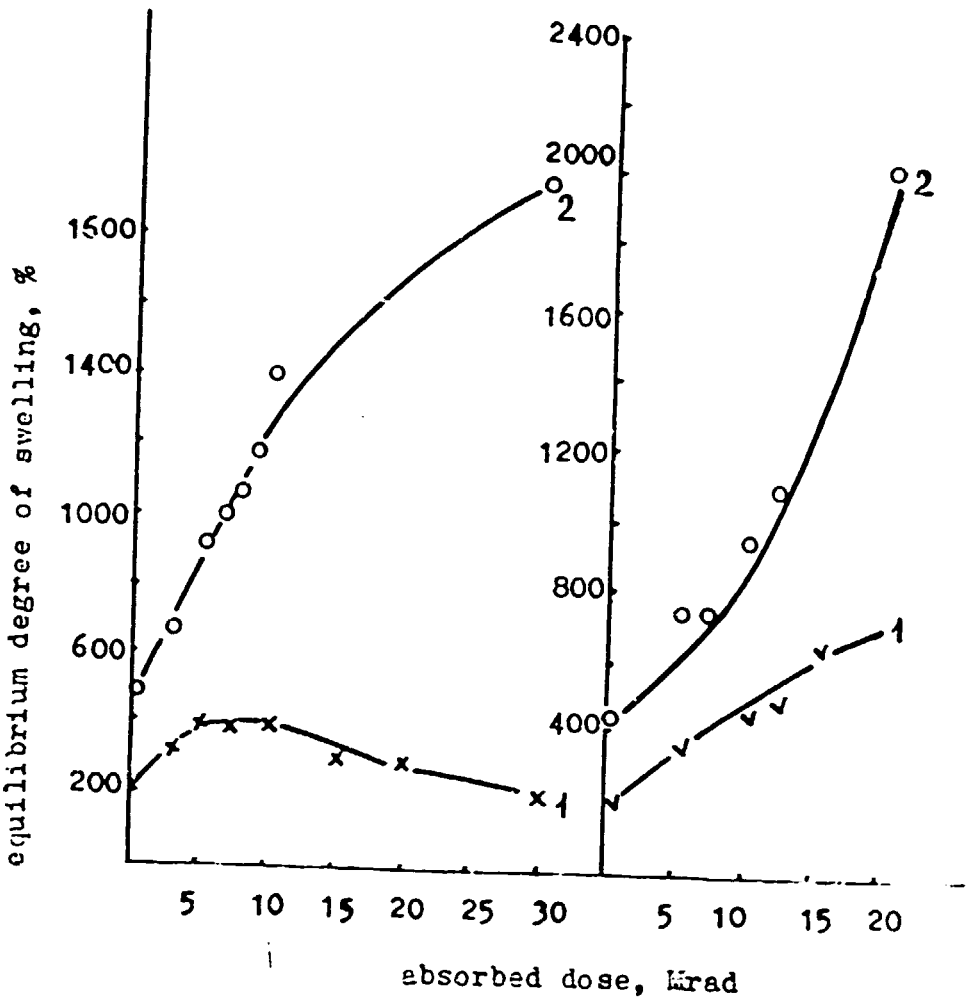


Fig.2. Variation of the equllibrium degree of swelling of the radiation breakdown products of bladders(a) and inner tubes(b) as a function of the absorbed dose value:

1 -with respect to the mass of the specimen after the removal of the solvent;

2 -with respect to the rubber substance content in the weighed amount after the removal of the solvent

Table 6

PROPERTIES OF RADIATION RECLAIM PRODUCED FROM BLADDERS AND INNER TUBES AT DIFFERENT ABSORBED DOSES AND PROPERTIES OF RECLAIM VULCANIZATES

Rubber compound type	Vulcanizing system type	Absorbed dose, Mrad	Mooney viscosity, units	Stress at 300% elongation, MPa (f_{300})	Tensile strength, Mpa (f)	Relative elongation,% (L)	Tear resistance, kN/m (G)	Equilibrium degree of swelling, %	Acetone extract, %	Chloroform extract, %
1	2	3	4	5	6	7	8	9	10	11
Bladder	Resin curing (I)	5	-	3.6	5.2	460	29	321	2.9	14.3
		10	-		scrap(pores,blisters)			400	4,1	25.8
	Resin curing (II)	5	-	4.3	5.5	400	31	313	3.3	11.9
		10	-		scrap(pores,blisters)			357	5.2	19.3
	Sulfur curing (I)	5	-		scrap(pores,blisters)			242	I.5	7.7
		10	-			id.		289	3.2	14.6
		15				id.		481	3.6	35.7
	Sulfur curing (II)	3	-	9.8	I2.6	380	25	-	-	-
		5	86	6.8	9.7	412	40	174	I.6	4.6
		7	56	6.I	7.9	384	36	192	I.7	5.4
		8	38	7.2	8.3	348	30	-	-	-
		9	36	6.2	6.7	340	29	-	-	-
		10	20	3.6	4.4	392	24	203	2.I	10.4
Inner tubes	Sulfur curing (I)	5			scrap(pores,blisters)			178	4.2	6.5
		10				id.		246	5.7	7.5
	Sulfur curing (II)	5	88	3.3	4.7	468	33	162	4.4	7.0
		7	90	3.0	4.8	476	27	179	4.6	6.6
		10	33		scrap(pores,blisters)			212	4.5	8.6
		12	-			id.		273	4.5	9.0

To determine Mooney viscosity of the reclaim obtained from bladders at the absorbed dose of 3Mrad was impossible due to its elevated stiffness and that of the reclaim from bladders and inner tubes at the absorbed doses over 10Mrad due to its tack.Because of the elevated tack we failed to prepare compounds for curing of the reclaim obtained at the absorbed doses over 15Mrad.

It should be noted that reclaim vulcanizates from bladders,especially resin ones,have defects,such as pores,apparently due to the increased content of gaseous products in the reclaim.

Bladder reclaim is better cured with sulphur:the strength properties of sulphur vulcanizates are higher than those of resin ones, and the equilibrium degree of swelling and chloroform extracts are lower.

Reclaim vulcanizates from inner tubes have the same external defects as reclaim vulcanizates from bladders,namely,pores and blisters.The presence of such defects can be related to the fact that the gaseous products of bladder/inner tube stocks radiolysis are not fully removed from the reclaim because of the low temperatures(max.40°C) at all stages of processing under laboratory conditions.

1.5. Effect of the radiation reclaim obtained from bladders on the properties of bladder/inner tube rubber stocks produced in the USSR

The reclaim content in the compounds was 10p.h.r.per 100p.h.r.of butyl rubber.The formulations are given in Appendices 1 and 2 correspond to the Chinese data in the composition of bladder and inner tube compounds.

The compounds were prepared on the basis of rubbers and ingredients of the Soviet make excluding the reclaim made from the Chinese bladders at the absorbed doses of 5,7 and 10Mrad.Preliminarily the reclaim was subjected to processing on the mills for 2 min.with the 1 mm nip between the rolls.

It can be seen from Tables 7 and 8 that the use of 10 parts of reclaim doesn't cause any significant change in the properties of the bladder and inner tube compounds.The greatest effect is produced by the reclaim obtained at 10 Mrad.Nevertheless the properties of the compounds containing this reclaim are within the limits of the values admissible for the bladder/inner tube compounds in the USSR.

We also investigated a possibility of using unmilled irradiated rubber crumb(devulcanizate)in compounds because in the case of the

positive results this could allow to simplify the process of the radiation reclaim production.

The strength properties of the compounds are given in Table 9.

Table 7

PROPERTIES OF BLADDER COMPOUNDS CONTAINING RADIATION RECLAIM (10 p.h.r. per 100 p.h.r. of butyl rubber)

Properties		absorbed dose, Mrad			
		-	5	7	10
Plasticity		0.291	0.257	0.286	0.265
Scorching, 130°C, τ_5, min		25.5	24.0	25.0	19.5
Physical-mechanical properties					
under normal coditions	f_{300}, MPa	9.4	9.2	8.6	9.0
	f, MPa	15.8	15.0	15.2	14.9
	L, %	492	482	506	504
	σ_{tear}, kN/m	55	53	49	49
Elasticity					
20°C		10	10	10	10
100°C		31	35	38	30
Hardness		72	72	72	73
Heat ageing, 180°C, 24 hours					
Modulus 300%	f_{300}, MPa	12.3	11.5	-	-
	K	1.3	1.21	-	-
Tensile strength, MPa	f, MPa	12.3	11.6	11.3	10.7
	K	0.78	0.77	0.75	0.72
Relative elongation, %	L, %	304	308	307	294
	K	0.62	0.64	0.60	0.58
Tear resistance, kN/m	σ_{tear}, kN/m	37	37	36	35
	K	0.67	0.70	0.73	0.71

Table 8.

PROPERTIES OF INNER TUBE COMPOUNDS CONTAINING RADIATION RECLAIM FROM BLADDERS(10 parts by weight per 100 parts of butyl rubber) .

Properties		absorbed dose,Mrad			
		-	5	7	10
Plasticity		0.338	0.317	0.316	0.312
Physical-mechanical properties under normal conditions: Modulus 300%	f_{300}, MPa	5.6	5.4	5.9	5.4
Tensile strength,MPa	f, MPa	13.8	13.3	12.7	12.7
Relative elongation,%	L, %	658	678	645	668
Tear resistance,kN/m	σ_{tear}, kN/m	64	64	64	58
Elasticity					
	20°C	11	10	10	10
	100°C	32	34	34	34
Hardness		71	68	68	66
Heat ageing , 130°C, 48 hours					
Modulus 300%	f_{300}, MPa	6.9	8.0	9.1	9.3
	K	1.23	1.48	1.61	1.72
Tensile strength,MPa	f, MPa	10.7	11.0	11.6	11.6
	K	0.80	0.83	0.91	0.91
Relative elongation,%	L, %	496	438	406	402
	K	0.75	0.65	0.63	0.60
Tear resistance,kN/m	σ_{tear}, kN/m	47	47	45	47
	K	0.73	0.73	0.70	0.81

Table 9

STRENGTH PROPERTIES OF BLADDER COMPOUNDS CONTAINING PLASTICIZED AND UNPLASTICIZED DEVULCANIZATE(10 parts by weight per 100 parts of butyl rubber)

Properties	Compound No.			
	1	2	3	4
Plasticity	0.238	0.230	0.248	0.309
Modulus 300, MPa	8.3	8.1	7.9	6.9
Tensile strength,MPa	15.3	14.5	13.5	14.1
Relative elongation,%	508	490	476	560
Tear resistance,kN/m	50	49	51	53

Compound 1 in Table 9 is a reference one without reclaim;compounds 2-4 contain plasticized and unplasticized devulcanizate obtained at the absorbed doses:

compound 2 .....7 Mrad (plasticized)
compound 3 .....7 Mrad (unplasticized)
compound 4 .....10 Mrad (unplasticized)

From this data one can see that unplasticized devulcanizate,obtained at the absorbed dose of 7 Mrad,causes a greater reduction of strength and relative elongation than application of the same devulcanizate but plasticized before.Cured plates of compound 3 have noticable inclusions of big particles.There is no such defect in the vulcanizates of compound 2 and also in those of compound 4 containing a more plastic devulcanizate obtained at the absorbed dose of 10 Mrad. In terms of strength properties the vulcanizates of compound 4 are superior to the vulcanizates of compound 3 made with a less plastic devulcanizate having higher strength properties.

From the data in Table 9 it follows that application of unplasticized irradiated devulcanizate in rubber stocks is, apparently, not advisable.

1.6. Selection of the optimum dose and manufacture of experimental lots of radiation reclaim from bladders and inner tubes for testing in China.

Selection of optimum doses was made on the basis of the analysis of the radiation reclaim properties given in Table 6, the reclaim behavior during processing and the reclaim effect on the properties of the rubber compounds containing it (Tables 7,8)

As it can be seen from Table 6 the sulfur vulcanizates of the reclaim produced at the absorbed doses of 3 to 5 Mrad poseas high physical-mechanical characteristics. However, due to the low plasticity of this reclaim there are difficulties in its processing on the mills. At first the crumb doesn't easily form skin, then the skin doesn't form a sheet properly on the roll. Processing of the reclaim obtained at the absorbed dose of 10 Mrad also entails difficulties because of the reclaim abherence to the rolls. There is no principle difference observed in the properties of the rubber compounds containing reclaim produced at 5, 7 and 10 Mrad . Proceeding from this and also from economical considerations 7 Mrad was selected as an optimum dose.

About 25 kg were prepared at the absorbed dose of 7 Mrad and some samples were prepared at the dose close to the optimum one, namely : about 25 kg at 5 Mrad and about 20 kg at 10 Mrad .

Taking into consideretion the insufficient physical-mechanical properties of the inner tube reclaim even at 5 Mrad , the 15 kg test piece was manufactured at the absorbed dose of 4 Mrad.

As the weight of each reclaim sample was insufficient for the efficient processing on the refining mills the reclaim processing was done on the laboratory mills $320\frac{160}{160}$. The weighed amount of the reclaim (about 400 g each) was plasticized for 3 minutes with a 1.5 mm nip between the rolls.

The properties of the reclaim samples sent to China for testing are shown in Table 10.

Table 10.

PROPERTIES OF THE RADIATION BUTYL RUBBER RECLAIM SPECIMENS SENT TO CHINA FOR TESTING

Rubber compound application	Absorbed dose, Mrad	Mooney viscosity	Equilibrium degree of swelling, %	Extracts, %		Tensile*) strength MPa	Elongation at break, %	Tear*) resistance, kN/m
				Acetone	Chloroform			
Bladder	5	120	336	3.9	20.0	11.6	376	35
	7	62	373	3.7	31.3	9.0	368	33
	10	42	418	4.13	37.1	7.7	336	30
Inner tubes	4	150	286	8.7	7.6	7.3	500	39

*)Sulfur curing as per Formulation II given in Table 1 .

The samples of the radiation butyl reclaim were tested in China according to the procedures adopted there. The obtained results are given in Annex No 3.

No estimation of these samples effect on the properties of rubber compounds was made in the Chinese Republic.

1.7. Production of an experimental - industrial lot of reclaim .

Proceeding from the results of the reclaim sample testing (see Annex 3) the Chinese counterpart has determined that the experimental - industrial lot of reclaim from bladders should be produced by the Soviet side at the absorbed dose of 6 Mrad.

The experimental - industrial lot (1.5 t) was produced under the following conditions :

electrtrons energy .....2.0 MeV
electron beam current .....10 MA
thickness of the irradiated
crumb layer .....10 mm
distance from the outlet
window foil to the material...100 mm

Processing of a part of the irradiated material on refining mills showed that even after 36 passings through the nip of the refining mills (0.2 mm) the material doesn't form a sheet.

Proceeding from this , the irradiated material was sent to the

Chinese Republic in the form of crumb.

Characteristics of the experimental - industrial lot :
Mooney viscosity ..... 56 ,
modulus 300% , MPa 6,1
tensile strength, MPa.....80
relative elongation, %.....390

Further below there are the results obtained in China when testing the experimental - industrial lot with the participation of TRI representatives .

1.8. Testing of the experimental - industrial lot of reclaim in the China

The irradiated material received from the USSR was subjected to mechanical processing in China as follows:

At the first stage there was mechanical processing on the mills with smooth rolls supplied with an apron.

The processing was done by 50 kg lots of crumb for 7-10 minutes with the 3-5 mm nip between the rolls.

At the second stage the milled material was subjected to double processing on the refining mills under the following conditions :

First pass :
the nip between the rolls ..... 0.5 mm
the roll temperature .....80°-100°C

Second pass :
the nip between the rolls ..... 0.2-0.3 mm
the roll temperature .....84°-100°C

After this mechanical processing the reclaim had the following parameters :

Plasticity 0.23
Moisture content, %.....0.1
Ash content, % 3.56
Acetone extract, % 4.56
Hardness 61
Tensile strength, MPa 7.3
Relative elongation, % 432

The Soviet and Chinese specialists have come to a conclusion that such reclaim meets the requirements that the quality of butyl reclaim

should meet (see Annex 3).

The reclaim was tested by Chinese specialists in a bladder formulation . 22 p.h.r. of butyl rubber were replaced by 22p.h.r. of radiation butyl reclaim. The quality of the obtained rubber stock with the reclaim was compared to the quality of rubber stocks based on 100 parts of butyl rubber. The results are given in Table 11.

Table 11 .

EFFECT OF THE RADIATION BUTYL RECLAIM OBTAINED AT THE ABSORBED DOSE OF 6 Mrad ON THE PROPERTIES OF BLADDER RUBBER STOCKS .

Curing conditions and rubber stock parameters	A Compounds based on 100 p.h.r. butyl rubber			B Compounds based on 78 p.h.r.butyl rubber and 22p.h.r. butyl reclaim		
Curing at 160°C , min	40	60	90	40	60	90
Hardness	68	70	72	64	70	74
Relative elongation, %	630	590	640	660	600	520
Tensile strength, MPa	12.4	12.5	12.8	13.9	13.5	14.
300 % modulus , MPa	5.9	6.0	6.1	5.7	7.5	9.
Residual elongation , %	22	22	20	18	32	24
Tear resistance , kN/m		51			59	
Heat ageing ratio (120°C , 21 h.)		0.781			0.891	
Bend testing (number of bends)		300 , 000 Type A			300 , 000 no changes	

It follows from the data in the table that in the bladder rubber compound formulation used in China the radiation reclaim obtained from worn-ont bladders at the absorbed dose of 6 Mrad can replace minimum 20 p.h.r. butyl rubber.

2. QUALITATIVE AND QUANTITATIVE COMPOSITION OF THE GASEOUS PRODUCTS OF BUTYL RUBBER STOCK RADIOLYSIS

Radiation breakdown of butyl rubber and its vulcanizates is accompanied by gas emission. Information about volatile product composition is important both for clarification of elastomer behavior under the action of ionizing irradiation and for evaluation of the ecological purity of this process. To solve these tasks a qualitive

and quantitative analysis for gaseous products of worn-out butyl rubber radiolysis under the action of ionizing irradiation was done.

A method of gas adsortion chromatography was selected for the analysis. Optimum conditions for separation of the resulting gaseous substances were found, their identification was done , and quantities of these products depending on the absorbed dose value were found

Methodology of the experiment

The weighed amount of ground rubber was put into a metal cell for radiation processing . The cell was a metal vessel with two unions for gas sampling. From the top the cell was shut by aluminium foil through which a beam of accelerated electrons fell on the sample. The gas volume in the cell was determined by the difference between the cell volume and the volume of the weighed rubber amount. The samples were exposed to radiation on the electron accelerator ILU - 6 :

electron energy ..... 2 MeV
electron beam current .....10 mA
conveyer belt speed .....11 cm/s
frequency .....50 Herz

The absorbed dose varied withir 5 - 20 Mrad.The irradiation was carried out in the presence of the air oxygen.

The analysis of gaseous products of radiolysis was carried out in terms of heat conductivity on the chromatograph LHM-7A with a detector. The carrier gas was helium. Separation of the gaseous products of radiolysis occurred in the columns filled with molecular sieves (ℓ = 2 m) and silica gel (ℓ = 1 m) with the use of chromatone N-AW-HMDS on which there was an immobile phase squolan applied in the quantity making 10% of the sorbent weight.

Identification of the radiolysis products was done by comparison of the components retention times of the analyzed compound and suppose individual substances.Methane and isobutene were used as standard substances.

The basis for calculation of concentrations of gaseous radiolysis products served the peaks areas of separated compound components on the chromatogram. The obtained concentrations of the radiation breakdown products were used to calculate the values of radiation - chemical outputs G - the number of gas molecules formed in the breakdown of the sample that had absorbed the energy of 100 eV.

$$G_{gas} = \frac{C \cdot 6.023 \cdot 10^{23} \cdot 100}{6.25 \cdot 10^{19}} \qquad \frac{\text{molecules}}{100 \text{ eV}}$$

where C is concentration of the product in M related to 1 g of substance and to the absorbed dose of 1 Mrad ;
$6.25 \cdot 10^{19}$ is energy in electronvolts, obtained by 1 g after absorbing the doze of 1 Mrad ;
$6.023 \cdot 10^{23}$ is Avogadro number.

By varying the adsorbent filling the column and the temperature conditions of the analysis we found optimal conditions for separation of the gas blend components of the rubber radiation breakdown products.

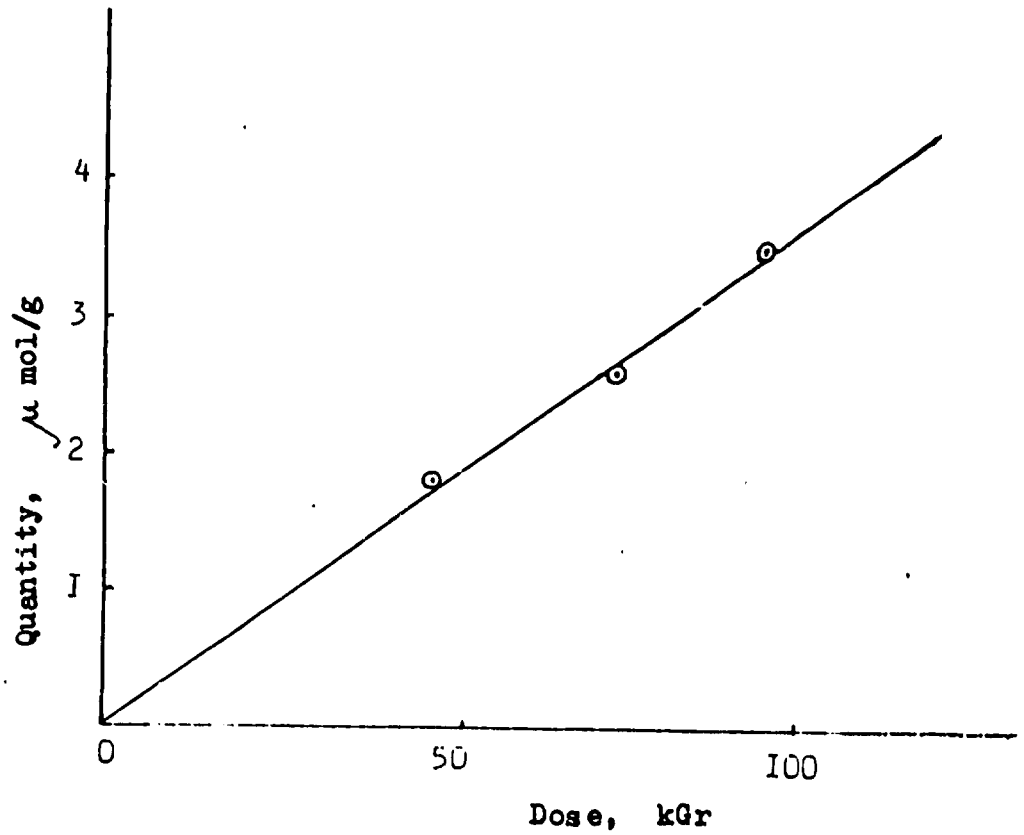
Qualitative analysis of the rubber stock radiolysis

Using the column with molecular sieves of NaX type at room temperature we observed five peaks on the chromatogram. It was found that they were hydrogen, oxygen, nitrogen, methane and carbon oxide.

Saturated and unsaturated hydrocarbons $C_2 - C_3$ are absent in the analyzed blend , which has been proved by the chromatograms recorded with the use of the column with NaX when the temperature is programmed up to 200° and also using the columns with silica gel and squolan. A peak of isobutene is registered on the column with silica gel at the column temperature of 100°C , and traces of carbon dioxide and isobutane at the temperature of 60°C.

Quantitative analysis of the radiolysis products of butyl rubber devulcanization

Proceeding from the obtained chromatograms depending on the value of the absorbed dose we found peak areas and calculated concentrations of the gaseous radiolysis products. Dependences of the resulting substance concentrations on the absorbed dose are shown in Figs. 3-6. As it can be seen from the given data the dose dependences have a different character. In the case of hydrogen, methane and carbon oxide the dependences of the concentrations on the absorbed dose have a linear character , whereas in the case of isobutene there is a sharp increase of the concentration with the growth of the absorbed value. It can evidence an increase of the radiation - chemical output of the product with an increase of the irradiation temperature since substantial heating up of the rubber samples under the beam of electrons at the doses over 10 Mrad has been established.



Fif.3. Dependence of the quantity of emitting hydrogen on the absorbed dose value.

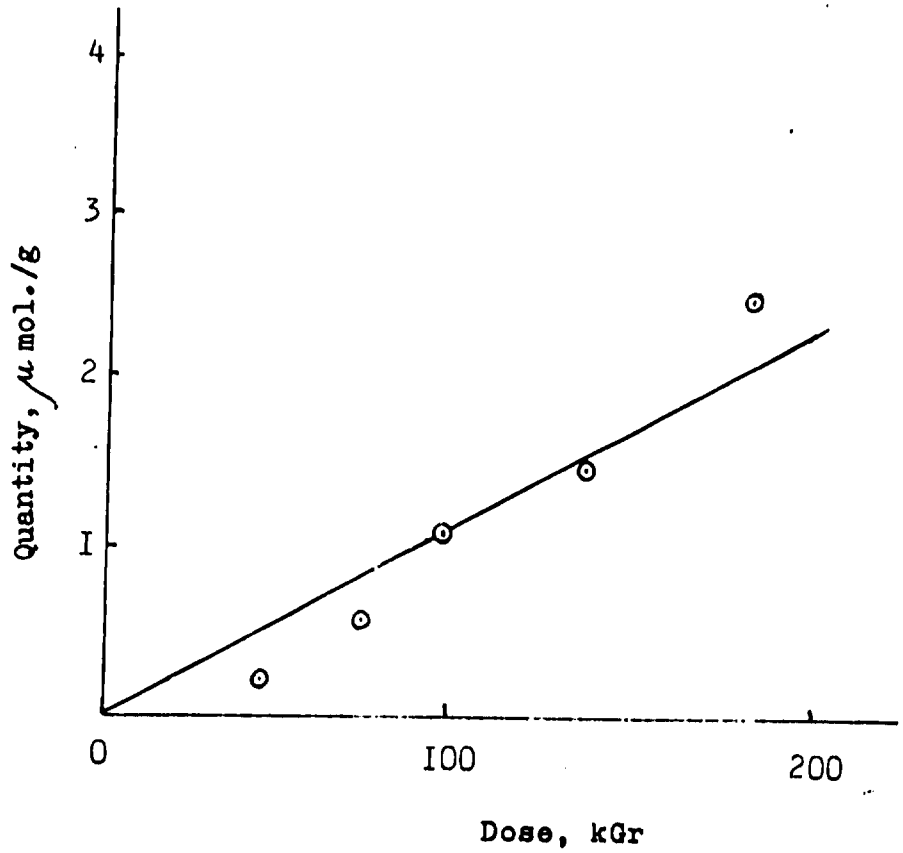


Fig. 4. Dependence of the quantity of emitting methane on the absorbed dose value

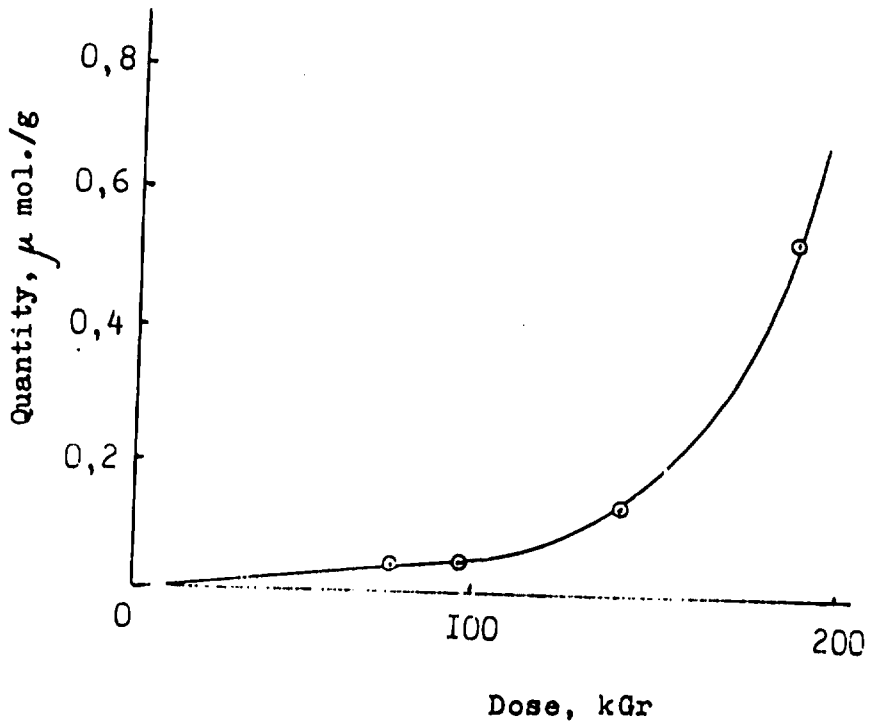


Fig. 5. Dependence of the quantity of emitting isobutene on the absorbed dose value

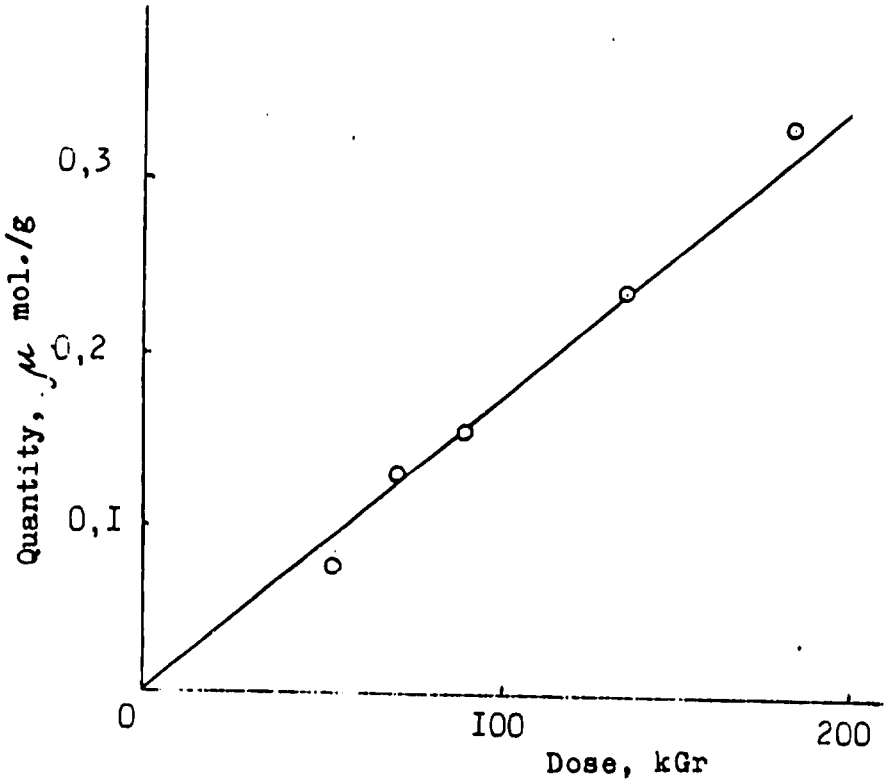


Fig. 6. Dependence of the quantity of emitting carbon oxide on the absorbed dose value

We estimated a degree of the cell heating up under the electron beam in real conditios of exposure (heat exchange with the environment, compressed air cooling of the cell , etc). It turned out that at the absorbed dose of 20 Mrad the temperature in it reached 90°C . Additionally it was checked that at this temperature there was no thermal breakdown of the butyl rubber vulcanizate. The increase of the isobutene concentration in the gas phase can also be associated with a low gas permeability of butyl rubber and hence with a retarded diffusion of this gas from the sample to the cell space.

The radiation - chemical outputs of the gaseous radiolysis products are calculated from the obtained concentration dependences. The obtained results are shown in Table 12 :

Table 12

RADIATION - CHEMICAL OUTPUTS OF THE RADIOLYSIS PRODUCTS

	H_2	CH_4	CO	iso-C_4H_8
G , $\frac{\text{molecules}}{100eV}$	0.36	0.12	0.0145	0.006
C , m^3 / t	0.073	0.020	0.002	0.001 (0.01)*

* Within the dose range of 15 - 20 Mrad

This table also gives the volumes of gaseous products in m^3, emitting from 1t. of worn-out rubber stocks at the dose of absorption 1 Mrad

The major products of the radiolysis are hydrogen and methane. Isobutene output in the dose range of 15 - 20 Mrad increases by an order of magnitude.

Nevertheless the amounts of substances emitting into the space of the working room cannot be of any danger.

3. TECHNOLOGY OF BUTYL RECLAIM PRODUCTION BY THE RADIATION METHOD FROM BLADDERS MADE IN CHINA AT THE PILOT PLANT

Bladder crushing

Worn-out bladders stored in an open asphalted or concrete area com to the crushing department where initially they are subjected to coarse crushing by means of a disc knife and a machine for coarse crushing.

Grinding of the resulting piecies of rubber with the size of about 150 x 150 mm to rubber crumb with the size of the particles of 7 mm maximum is done on the grinding mills with ribbed rolls using a water solution of surfactants to avoid agglomeration of the rubber. Having passed through the mills the partially ground rubber is fed to a one--tier vibratory sieve. The tailings from the sieve go back to the nip of the rolls;the sieve fraction containing up to 15% moisture is fed into a pneumatic drier. Drying of the rubber crumb proceeds till the residual humidity content becomes 1% maximum.

Devulcanization of rubber

From the hopper with a rotating bottom via a continuously functioning metering device the rubber crumb is fed to the hopper mounted over the feeding mills designed for compacting the rubber crumb. From the hopper the rubber crumb goes continuously to the nip where it is compacted and then goes to a transportation device passing under the electron accelerator scan. Devulcanization is effected by the action of accelerated electrons on the rubber vulcanization network. Irradiation of the rubber takes place on the drum provided with water cooling. The absorbed dose can vary within a wide range. The velocity of transportation is determined by the value of the absorbed dose.

Mechanical processing of the devulcanizate

Depending on the value of the absorbed dose and the application of the irradiated material there may be different ways of its processing.

a) processing on the mixing mills with an apron

The devulcanizate is fed by portions (by 50 kg) onto the mixing mills supplied with an apron and is milled for 5-7 minutes depending on the absorbed dose quantity. Then the milled devulcanizate undergoes processing on the refining mills: first on the semi-finishing ones (the sheet gauge is 0.4 - 0.5 mm) and then on the final ones (the sheet gauge is 0.2 - 0.3 mm). The reclaim sheet is wound up into rolls or wrapped around the drum from which it is cut off as a briquet.

Such processing is recommended for the reclaim obtained at the absorbed doses of 5 - 7 Mrad.

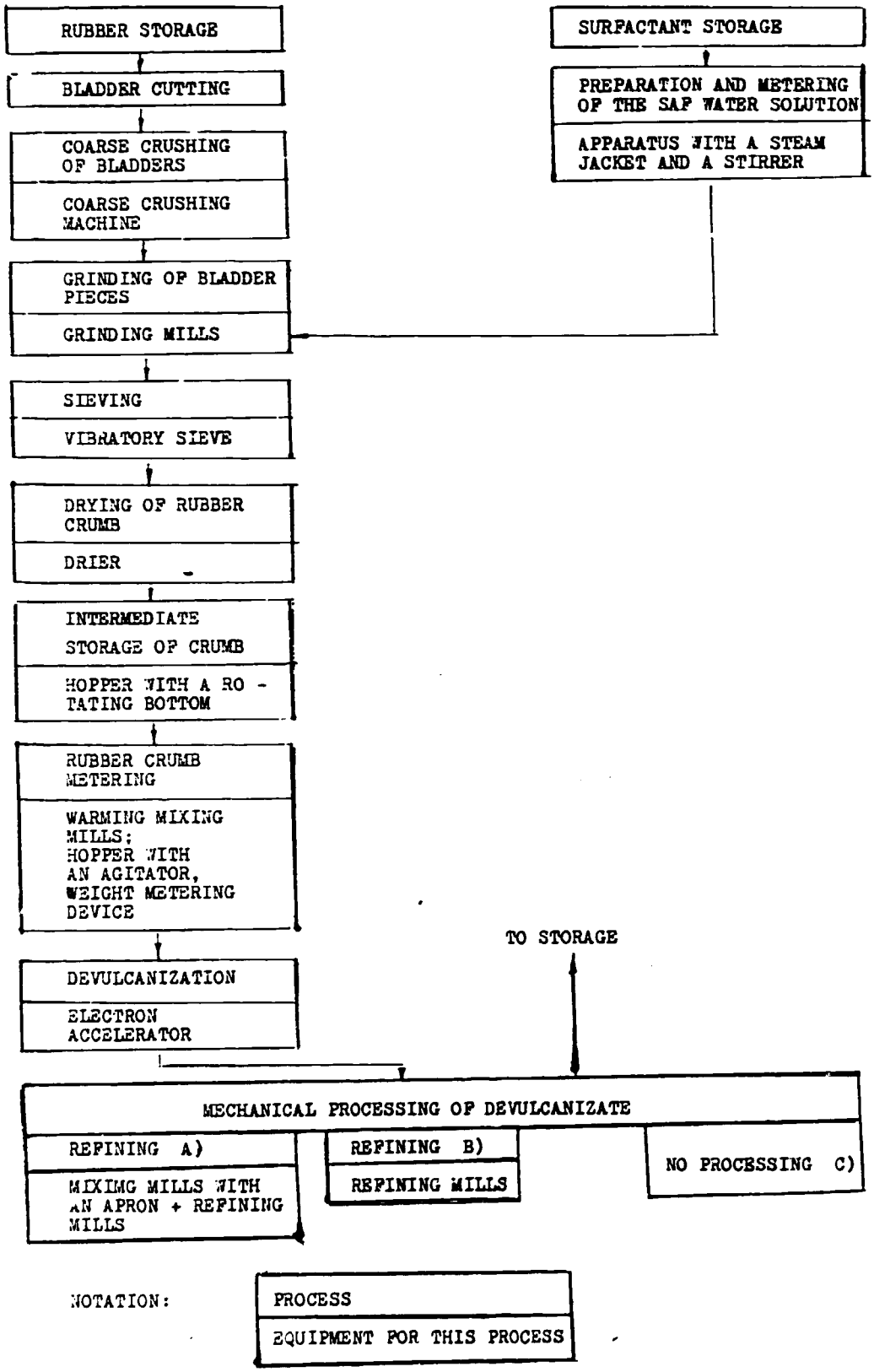
b) processing on the refining mills

Practical experience shows that the material obtained at the absorbed doses of 9-12 Mrad is plastic enough to be only processed on the refining mills.

In some cases depending on the absorbed dose and application it is

F L O W C H A R T

PRODUCTION OF RADIATION BUTYL RECLAIM



possible to eliminate the stage of mechanical processing of the devulcanizate. Then the irradiated crumb is packed into polyethylene bags which are sealed off and sent to the consumer.

CHARACTERISTICS OF THE STANDARD EQUIPMENT

No	Equipment and its function	Characteristics	Output, t / h
1.	Enamelled cast iron reactors for preparation and metering of SAF solution	Capacity.....630 and 1,250 l Working medium in jacket - - steam. Operating steam pressure in jacket..... 1 atm.	1.
2.	A disc knife to cut bladders	Disc knife diameter.....750mm Distance between knives.....150mm Disc rotation frequency.....405min Electric motor power....13kwt	2.5 -1.
3.	Coarse crushing machine	Dimensions of charging opening.....1,260 x 400 mm Overall dimensions.....3,000 x 2,200 x 3,000mm Electric motor power....134kwt	3,0
4.	Grinding mills for obtaining rubber crumb of required grinding	Roll length.....800mm Roll diameter.....550mm Friction.....1:3.08 Electric motor power....160kwt	0.35
5.	Vibratory sieve for sieving rubber crumb	Slope angle.....4°30' Number of double vibrations .....265 per min. Overall dimensions.....3,110 x 1,412 x 870 mm Electric motor power.....1.7kwt	0.35
6.	Electron accelerator ILU-6 for rubber devulcanization	Power .....20kwt Electron energy....1.5-2.0 MeV Weight.....2,200 kg Overall dimensions.....3,300 x 1,230 x 1,534 mm	0.28
7.	Refining mills for mechanical processing of devulcanizate	Roll length.....800 mm Roll diameter.....550 mm Friction.....1:1.87 Electric motor power.....75 kwt	0.35
8.	Mixing mills with apron for mechanical processing of devulcanizate	Roll length.....1,200 mm Roll diameter.....400 mm Friction.....1:1.27 Electric motor power...55kwt	
9.	Hopper with rotating bottom for intermediate storage of crumb	Crumb volume.....4.7 m^3	

ESTIMATED COST OF EQUIPMENT

No	Equipment	Number of units	Unit price, doll	Total cost, doll
1.	Cast iron reactor	2	1,670	3,340
2.	Disc knife	1	5,550	5,550
3.	Coarse crushing machine	1	69,440	69,440
4.	Grinding mills	1	23,330	23,330
5.	Vibratory sieve	1	2,780	2,780
6.	Electron accelerator	1	950,000	950,000
7.	Refining mills	2	16,670	33,340
8.	Mills with apron	1	16,670	16,670
			TOTAL:	1,104,450

CHARACTERISTICS OF THE OPTIONAL EQUIPMENT

Feeding and transporting device for feeding the rubber stock into the irradiation zone.

Function : feeding the crumb into the irradiation zone and transportation of the irradiated material out of it.

Requirements :

Provision of synchronization and smooth adjustment of the velocity of the rubber crumb coming into the nip, feeding it under the accelerator scan and taking the irradiated material out of the accelerator chamber.

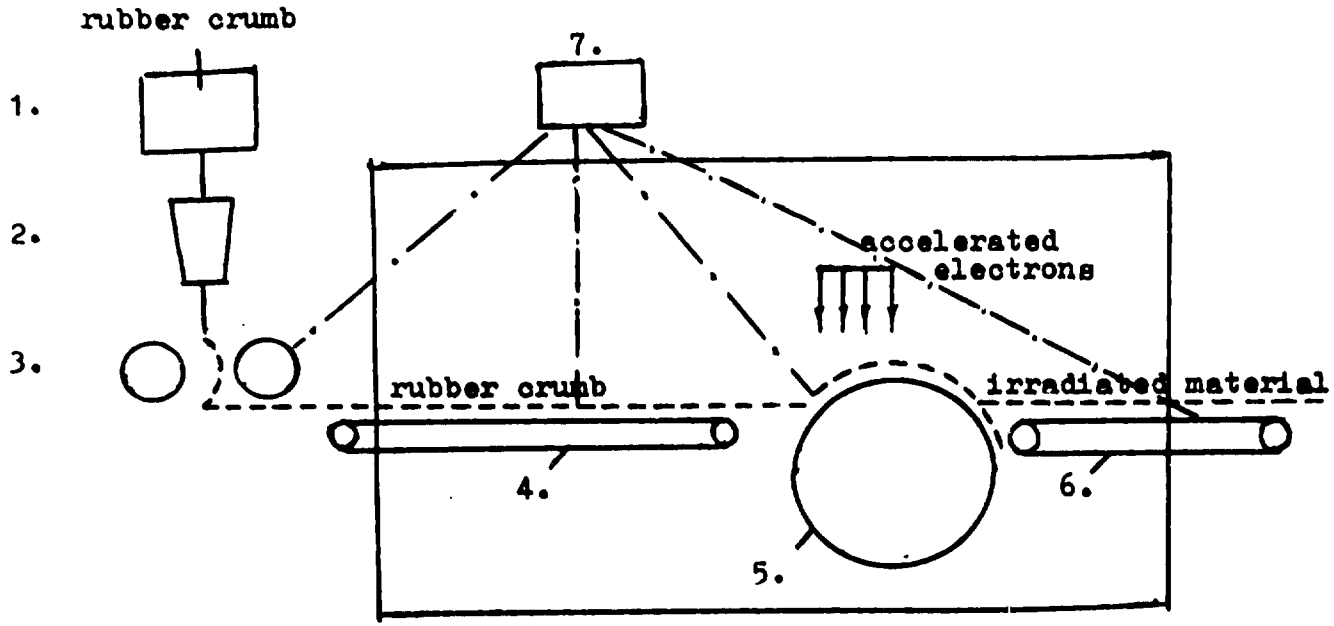
GENERAL CHARACTERISTICS OF THE EQUIPMENT COMPONENTS

No	Equipment	Characteristics	Special features
1.	Hopper over feeding mills	Discharge opening length- - 550 mm Discharge opening width- - 20 mm Side wall slope angle- - 55 °	The hopper must be provided with a vibrator to prevent crumb bridging

No	Equipment	Characteristics	Special feature
2.	Feeding mills	Roll working part diameter - - 315 mm Roll length - - 630 mm Electric motor power - - 20 kwt Overall dimensions - -2,985 x 1,535 x 1,565 mm	
3.	Conveyers	Belt Material - stainless steel Width - 800 mm	Conveyers must b supplied with li ting side bars prevent rubber/ devulcanizate sliding from the
4.	Drum	Diameter - 1,000 mm Length - 800 mm Material - stainless steel Electric motor power-2kwt	The drum must ha limiting bars an a removable knif along the entire length.
5.	Metering device for rubber crumb	Metering limits - 200 - 750kg/h Electric motor power - 1 kwt	

SCHEMATIC DIAGRAM

Feeding and transportation device for feeding rubber into irradiation zone



1. Metering device for rubber crumb
2. Distributing bin
3. Rubber crumb compacting mills
4,6. Conveyers
5. Drum
7. Regulator device

Drying unit

Function : rubber crumb drying.

Requirements : Provision of the residual humidity in the dry crumb 1% maximum.

Principle of action : drying of the crumb in suspended state by the flow of hot air.

General parameters of the drying process

Crumb humidity, %

initial.....under 20

final.....1 maximum

Air temperature, °C

at the drier inlet.....140-160

at the drier outlet.....50-60

Wet crumb dwell time in the drier, min.....3±0.1

As a rule, the dimensions of the working chamber and the accelerator room are determined by the overall dimensions and the lay-out of the processing equipment.

Common dimensions of the working chamber and the accelerator room are usually made practically the same and have an area of 8 x8m. For these two rooms it is most convenient and rational to install the accelerator at the height of 2.2+2.7 m from the floor of the working chamber. The frame for the accelerator installation is covered on the top by a steel shield with a round hole of 1250 mm in diameter.

When concrete is used the wall thickness in the working chamber should provide for attenuation of the braking radiation of the accelerator in the area of the energy 2 MeV by 10^7 times (the dose rate 2 x 10^{-3} rad/h).

The construction of the channels going through the shielding should ensure the exposure rate not higher than the permissible level in all point, achievable by the personnel operating the equipment.

The output of the radiation plant for processing a monolith material can be calculated by the formula:

$$A = \frac{360 \cdot W \cdot \eta}{D} \text{ kg/h}$$

where

W is radiation power, kwt

D is a required radiation dose, Mrad

η is a radiation utilization factor, fractions of a unit

In the case of the accelerator ILU-6: W = 18 to 20kwt (average-19kwt)

$\eta = 0,5$

At the absorbed dose of 5 Mrad the output for processing monolith rubber is

$$A = \frac{360 \cdot 19 \cdot 0.5}{5} = 680 \text{ kg/h}$$

Since bladder rubber is irradiated as crumb whose density is 30% of the monolith rubber density, the output of the pilot plant for radiation processing of the bladder crumb by the absorbed dose of 5 Mrad will be:

$$A = 680 \cdot 0.3 \approx 200 \text{ kg/h } (0,2 \text{ t/h}).$$

According to item 16 page 10 of the Report the maximum annual fund of the plant operation time has be

$$365 \times 24 \times 0.75 = 6570 \text{ h.}$$

and the maximum output of the plant at the absorbed dose of 5 Mrad is

$$6,570 \times 0.2 \approx 1,300 \text{ t/year}$$

4. GROUNDS FOR TECHNICAL/ECONOMIC EXPEDIENCE OF INSTALLING A PILOT PLANT FOR PRODUCTION OF BUTYL RECLAIM BY THE RADIATION METHOD IN CHINA;

4.1 Technical expedience of a pilot plant

A pilot plant in the Chinese People's Republic is necessary for solving the following technical problems on it:

1) Development of an industrial technology for reclaim production
2) Production of representative experimental lots of reclaim and running of extended production trials of bladders made with the use of the reclaim.
3) Determination of economic characteristics of the plant operation with the aim of an unbiassed economic estimation of the production and application of butyl reclaim.
4) Production of reclaim at different absorbed doses and its testing in rubber compounds of different types and also for making building materials and articles.
5) Elaboration of specifications for radiation butyl reclaim (depending on its application).
6) Search for and testing of equipment permitting to obtain rubber crumb from bladders without the use of water surfactants solutions (simplification of the flow chart for producing rubber crumb from

bladders).

4.2. Economic efficiency of radiation butyl reclaim application.

The maximum output of the pilot plant for producing reclaim at the absorbed dose of 5 Mrad is 1,300 t reclaim annually which is determined by the maximum capacity and operation time of the electron accelerator ILU-6 and also by the compactness of the processed crumb.

Due to the absence of initial Chinese data required for calculation of economic efficiency of application of butyl reclaim, which can be achieved with the pilot plant in China, the calculation was made procceding from the conditions existing in the USSR.

Taking into account the cost of initial materials, transportation and handling expenses, wages and salaries, deductions for social insurance, the cost of mastering and preparation of the production, maintenance and operating expenses, shop/factory and other production costs, the manufacturing cost of 1 t butyl reclaim produced at the pilot plant will be 640 doll/t.

The price of butyl rubber is 1,990 doll/t.

The economic effect of replacing 1 t butyl rubber [illegible] t butyl reclaim will be 1,260 doll/t.

The cost of the principle equipment of the plant is about 1.104 million dollars.

The cost of the optional equipment is about 10% of the principle equipment cost, i.e. 0.110 million dollars.

The total cost of the equipment is 1.214 million dollars.

From the experience of the Soviet Union it is known that the cost of the equipment makes about 70% of the entire plant cost.

Hence, the cost of the pilot plant will be 1.734 million dollars.

5. ECOLOGY

Worn-out bladders of curing presses are referred to such wastes of the tyre manufacture that have not found efficient secondary application for a long time. As a rule, they are buried or burnt on industrial dumps. Obtaining of radiation reclaim from worn-out bladders can be considered to be one of the possible solutions of this problem.

Soft temperature conditions and absence of reclaiming agents make this method more clean ecologically compared to such conventional production methods as thermomechanical and water-neutral ones. Reclaiming of rubbers in a water medium is accompanied by a great amount of effluent water polluted with softeners residues and small particles of rubber. With a high-temperature thermomechanical method, devulcanization is accompanied by releasing into the atmosphere products of oxidation and thermal breakdown of rubbers and reclaiming agents, including such agressive ones as sulphur oxides and phenols.

There are no wastes of this kind when reclaim is obtained by the radiation method. The main harmful effluent is ozone formed as a result of air radiolysis in the target room.

Characteristics of wastes at different production stages

1) Crushing with the use of water solutions of surfactants - crumb removed by the ventilation. There is no formation of polluted waste water during crushing.

2) Drying of rubber crumb - small crumb removed by the ventilation; water vapors.

3) Devulcanization.

There are two different sources of pollutions in vulcanization:
a) formed as a result of rubber irradiation and
b) due to the air radiolysis in the target room.

As it follows from the data given in the Report, during rubber exposure the chemical-radiation transformations of the vulcanization network result in formation of carbon oxide CO, methane CH_4, hydrogen H_2, isobutylene (chemical-radiation outputs of these products at the absorbed dose of 10 Mrad are 0.002; 0.12; 0.073; 0.001 m^3/t, respectively).

Accelerated electrons affect the ambient air to form ozone and nitrogen oxide.

4) Refining - kaolin dust, carbon oxides.

Thus, the process of making radiation butyl reclaim is accompanied by the release of suspended substances and insignificant (excluding ozone) amounts of gaseous harmful substances into the environment.

Environmental protection

80% of suspended harmful substances released into the atmosphere are trapped be a system of cyclones. The trapped rubber crumb is completely returned to the process.

Catalythic decomposition of ozone in a special reactor is envisaged to clear the air in the target room. The amount of the remaining resulting gases per unit of the air volume is lower than the permissible limit concentrations adopted in the USSR. Besides, their thinning with the ventilation air occurs continuously. Thus, the gas content in the released air does not exceed the permissible limit concentrations (in the USSR): for ozone 0.1 mg/m^3; for nitrogen oxides 5 mg/m^3 ; for aliphatic hydrocarbons 90 mg/m^3.

CONCLUSIONS

A technology for production of radiation butyl reclaim from bladder rubber stocks made in China with the use of an electron acccelerator ILU-6 was de-veloped. The basis for this was a research carried out in the following directions:

- estimation of the high-energy radiation on the structure and properties of butyl rubber stocks produced in the Chinese People's Republic;
- determination of the composition of the gaseous products of these rubbers radiolysis;
- refinement of the dosimetry methodology and determination of the absorbed energy distribution of fast electrons in rubber crumb;
- refinement of the methods for crushing bladders and inner tubes on the laboratory/industrial equipment;
- production of experimental and enlarged lots of butyl reclaim from bladders at the selected optimum absorbed dose;
- determination of technologial parameters for processing of irradiated rubber.

Proceeding from the obtained data a selection of the technological equipment was done and a flow chart of the plant for production of radiation butyl reclaim from Chinese bladders was developed.

Applications of the radiation butyl reclaim from bladders were defined. It was established that the reclaim obtained at the absorbed dose of 6 Mrad can replace up to 20 p.h.r. butyl rubber in the formulation of Chinese bladder stocks. The use of this reclaim in butyl inner tubes is also possible. The estimated economic effect of using 1 ton butyl reclaim in the bladder formulation is 1260 dollars.

An estimation of the ecological cleanliness of the radiation reclaiming method shows that in the radiation butyl reclaim production there are no wastes typical of other reclaiming methods. The main harmful effluent can be ozone that is a product of the atmospheric oxygen radiolysis in the target room. The content of ozone in the ventilation air can be easily reduced down to permissible limit concentrations by way of its catalytic breakdown in a special reactor.

It should be noted that the flow chart developed for this reclaiming process is flexible enough, and the adopted technical/techno-

logical solutions can be easily modified if it is required by considerations of the economic and technical expedience.

Annex 1

FORMULATION OF THE BUTYL RUBBER BLADDER COMPOUND AND CONDITIONS OF ITS PREPARATION

Ingredients	Content of ingredients in rubber compound, p.h.r.	
	without reclaim	with reclaim
Butyl rubber BK- 1675-T	100	100
Nairit KR- 50	5	5
Reclaim	-	10
Zinc oxide	5	5
Stearic acid	3	3
Stabiloil-18	-	5
Carbon black PM -100		55
Resin SP-1045	12	12
TOTAL	185	195

	Rotational speed of rotor, r.p.m.	Time of manufacture, min	Dumping temperature, °C
Stage 1	80	7.5	at least 180
Stage 2	60	3.0	up to 110

Annex 2

FORMULATION OF THE BUTYL RUBBER INNER TUBE COMPOUND AND CONDITIONS OF ITS PREPARATION

Ingredients	Content of ingredients in rubber compound, p.h.r.	
	without reclaim	with reclaim
Butyl rubber БК-1675-T	100	100
Reclaim	-	10
Zinc oxide	5	5
Stearic acid	1	1
Altax	0.5	0.5
Thiuram	1	1
Sulfur	2	2
Stabiloil - 18	20	20
Carbon black PM-50	25	25
Carbon black PM-100	25	25
TOTAL	179.5	189.5

	Rotational speed of rotor, r.p.m.	Time of manufacture, min	Dumping temperature, °C
Stage 1	80	6	at least 160
Stage 2	60	2	up to 110

Annex 3

RESULTS OF TESTING EXPERIMENTAL SAMPLES OF RADIATION BUTYL RECLAIM IN CHINA

(from inner tubes - 4 Mrad, from bladders - 5,7 and 10 Mrad)

	Dose, Mrad											
	C_1 (4)			C_2 (5)			C_3 (7)			C_4 (10)		
Cure time,min.	30	40	60	30	40	60	30	40	60	30	40	60
Hardness	52	52	52	66	68	68	68	69	70	67	69	70
Strength,MPa	8.0	8.1	7.6	8.0	7.8	8.1	5.7	5.3	5.9	3.9	4.4	4.6
Relative elongation, %	620	640	600	528	532	524	504	448	472	452	492	484
Plasticity		0.124			0.472			0.461			0.553	
Flexibility		5.79			3.78			3.19			2.72	
Recovery		2.25			1.11			0.74			0.30	

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