

Exxon™ butyl rubber

ExxonMobil

Exxon™ butyl rubber innertube technology manual

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Abstract

Many bias and radial tires have innertubes. Radial truck tube-type tires are particularly common, and in many instances, such as in severe service, off-road applications, are preferred over tubeless radial tire constructions. The technology requirements for tubes for such tires is, in many respects, equally demanding when compared to that for the tire and wheel in the assembly. This manual has been prepared to describe how butyl rubber is important in meeting the demanding performance requirements of tire innertubes. Representative innertube compound formulations and compound properties are discussed along with typical processing guidelines of the compound in the manufacture of innertubes.

Chlorobutyl rubber based compound formulations are also used in innertubes. Such innertubes show good heat resistance, durability, allow greater flexibility in compounding, and process equally well as regular butyl rubber tube compounds.

An extensive discussion of bicycle tire innertubes has been included. Service conditions can range from simple commuting and recreation to high speed competitive sporting applications. Like automobile and truck tire innertubes, tubes for bicycle tires can thus have demanding performance requirements.

Guidelines on troubleshooting provide a checklist for the factory process engineer to enhance manufacturing efficiency, high quality, and meet the end-product performance requirements. A set of references for further consultation conclude the manual.

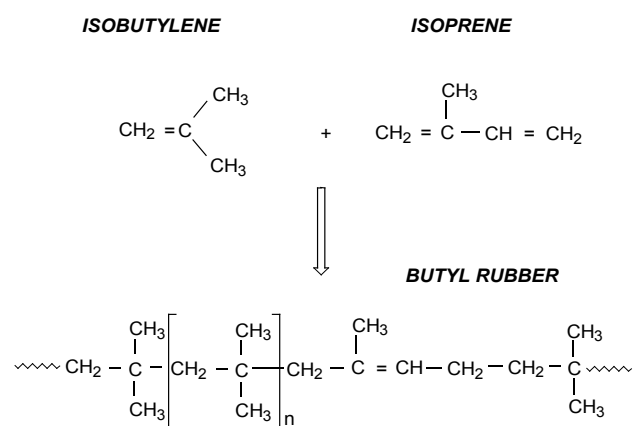
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1. Introduction

Butyl rubber (IIR) is a copolymer of isobutylene and a small amount of isoprene (Figure 1)^{1,2}. The primary attributes of butyl rubber are excellent impermeability for air barrier performance and good flex fatigue properties. These properties result from low levels of unsaturation in between the long polyisobutylene chain segments. Tire innertubes were the first major use of butyl rubber, and this continues to be a significant market today.

Figure 1

Butyl rubber: poly(isobutylene-co-isoprene)^{1,2,3}



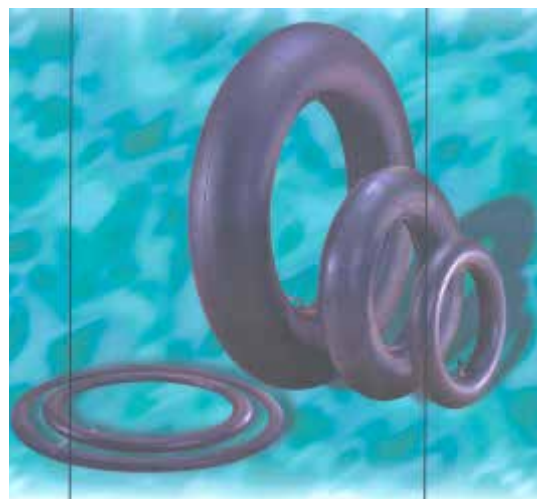
In the most widely used manufacturing process for butyl elastomers, a slurry of fine particles of rubber dispersed in methyl chloride is formed from isobutylene and isoprene, in a reactor after Lewis acid initiation. The reaction is highly exothermic, and a high molecular weight can be achieved by controlling the polymerization catalyst level and temperature, which is typically between -90°C to -100°C. The most common polymerization process uses methyl chloride as the reaction diluent and boiling liquid ethylene to remove the heat of reaction and maintain the low temperature needed. The final molecular weight of the butyl rubber is determined primarily by controlling the catalyst level, temperature, and initiation and chain transfer reactions. Water and oxygenated organic compounds that can terminate the propagation step are minimized by purifying the feed systems.

The chloro and bromo derivatives of butyl rubber were introduced commercially in the 1950s and early 1960's. Due to butyl rubber's low air and gas permeability, a large proportion of the world's tube-type pneumatic tires, from bicycle and passenger car to truck and earthmover tires, rely on butyl rubber innertubes to retain air pressure. Figure 2 illustrates various types of butyl rubber innertubes^{2,3,4}.

Of the many properties of butyl rubber, low permeability to gases is among the most important. Tables I and II illustrate some of the properties of both butyl rubber and compounded butyl rubber, and compare the properties of butyl rubber to other elastomers such as natural rubber, styrene butadiene rubber (SBR), and special purpose elastomers^{2,5}. Tire inflation pressure retention is now clearly recognized as a very important parameter in maintaining tire operating performance, ensuring low tire rolling resistance and minimize vehicle fuel consumption, and ensuring long tire life by maintaining a proper tire tread footprint. The air retention properties of butyl rubber innertubes contributes toward attaining these properties.

Figure 2

Examples of butyl innertubes



Ref: ExxonMobil data.

Table IPhysical properties of butyl rubber²

Property	Value	Composition ^a
Density, g/cm ³	0.917 1.130	B CBV
Coefficient of volume expansion (1/V) (V/T), K	560 x 10 ^{''} 460 x 10 ^{''}	BV CBV
Glass-transition temperature, °C	-75 to -67	B
Heat capacity, Cp kJ/(kg.K) ^b	1.95 1.85	B BV
Thermal conductivity, W/(m.K)	0.130 0.230	BV CBV
Refractive index, np	1.5081	B

(a) B = butyl rubber; BV = vulcanized butyl rubber; CBV = vulcanized butyl rubber with 50 phr carbon black.

(b) To convert J to cal, divide by 4.184

In addition, butyl rubber has good heat, oxygen and ozone resistance as well as good dynamic properties which enhance the long-term durability of innertubes. This is important given

common stringent operating conditions such as long-distance travel at higher operating speeds, and heavier payloads under difficult weather and temperature conditions. This manual provides a review of the current butyl rubber and chlorobutyl rubber innertube technology. It also discusses basic technology on compounding, processing, and troubleshooting.

Table II

Permeability of various elastomers to gases at 25°C relative to natural rubber gum vulcanizates (=100)⁵

Elastomer	He	H ₂	O ₂	N ₂	CO ₂	Air
Silicone Rubber		1070	2200	3300	1600	2700
Natural Rubber	100	100	100	100	100	100
EPDM			88	80	66	83
Polybutadiene		86	82	80	105	81
SBR	74	81	73	78	94	76
NBR (80/20 butadiene acrylonitrile)	55	51	35	31	48	33
NBR (73/27 butadiene acrylonitrile)	39	32	17	13	24	15
Polchloroprene		27	17	13	24	15
NBR (68/32 butadiene acrylonitrile)	32	24	10	7.5	14	8.5
Butyl Rubber	27	15	5.6	5.0	4.0	4.8

Note: 1. Lower rating is better.
2. Permeability at 25°C.
3. See Appendix 1 for abbreviations.

2. Innertube application requirements

The innertube of a pneumatic tire assembly has a number of performance requirements which include:

- Retention of air pressure during the tire and innertube service life (low air permeability).
- Durability (oxidation, ozonolysis, heat, and aging resistance).
- Tear resistance.
- Low growth (low tension set) during service.
- Non-stickiness of the innertube to the tire casing during service (heat resistance & retention of physical properties).

Butyl rubber innertubes can meet all of these performance criteria much better than innertubes made from general purpose elastomers such as natural rubber as illustrated in the Figures 3, 4, 5, and 6.

Permeability of butyl elastomers

Among hydrocarbon elastomers, isobutylene based rubbers (butyl and halobutyl) show very good impermeability to air and other gases (Table II, Table III). The permeation of a gas through a polymeric membrane involves dissolving of the gas in the polymer at the high-pressure side, diffusion through the membrane, and evaporation at the low-pressure surface. Under a given steady state condition, the rate of transfer of gas through the membrane (i.e. permeability) is governed by the solubility and diffusivity of the gas. The diffusion coefficient or diffusivity defines the rate of migration of the gas molecules under this concentration gradient. The permeability coefficient, Q , is equal to the product of the solubility and diffusivity.

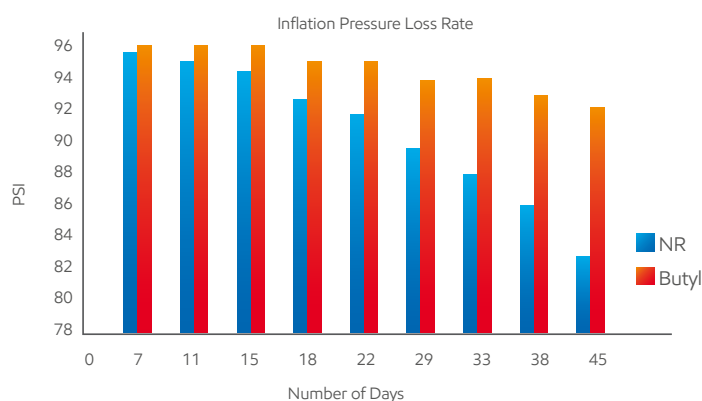
Table III

Relative air permeability of commercial elastomers⁶
(polymer, carbon black 80phr, stearic acid 2phr, processing aids & oils 14phr, ZnO 5phr, cure system varies)

Compound	1	2	3	4	5
Exxon™ Butyl 268	100				
Exxon™ Chlorobutyl 1066		100			
SBR 1502			100		
Exxon Vistalon™ EPDM				100	
Natural Rubber					100
Air Permeability (Q) 24°C	0.32	0.34	3.06	4.05	4.36

Figure 3

Effect of permeability on air retention



The solubility of gases in butyl rubber is similar to that in other hydrocarbon polymers, but the rate of diffusion through isobutylene based elastomers is much lower. This is due to the highly packed polyisobutylene molecule which has the smallest coil dimension of the polyolefins. The resulting efficient intermolecular packing of polyisobutylene leads to a low free volume fraction (high density) and thus low permeability values. This low degree of permeability to gases explains the preferred use of butyl and halobutyl rubbers for the manufacturing of innertubes and tire innerliners.

Figure 3 illustrates the low permeability to gas of butyl and natural rubber, showing that butyl rubber is much superior. Hence, tires with butyl rubber innertubes are better at retaining air pressure.

Heat resistance

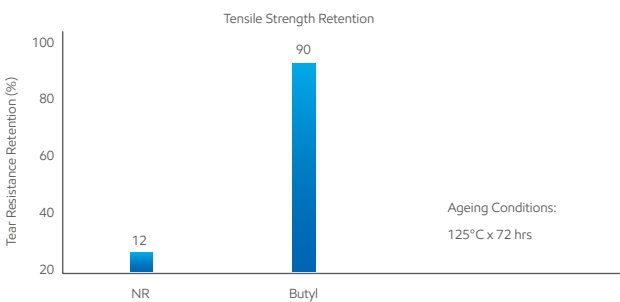
Innertubes made from butyl rubber are more durable than those made with natural rubber, as butyl rubber is better able to retain its properties at high temperatures. Figure 4 compares a natural rubber innertube to a butyl rubber innertube after a tire dynamometer durability test (run at 50km/hr for 357 hrs). It was found that the natural rubber innertube degraded and adhered to the inner wall of the tire. In contrast, the butyl innertube on completion of the tire dynamometer test showed much less degradation.

Figure 4

Butyl innertube tensile strength retention after aging



Ref: ExxonMobil Company data

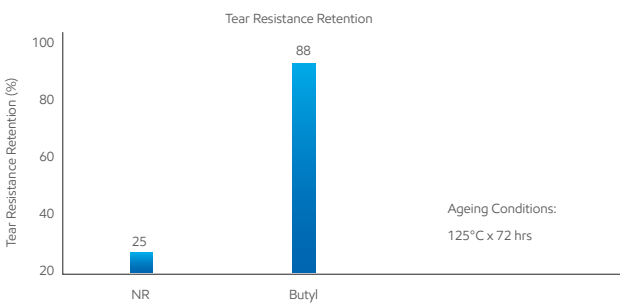


Tear strength

Due to the molecular structure, butyl rubber has better aged tear strength retention when compared to natural rubber (Figure 5). Less tearing can influence the magnitude of punctures and reduction of puncture size which may minimize repair work. Rapid air loss can be diminished as pressure loss is slower and punctures may not grow as rapidly.

Figure 5

Butyl and natural rubber tear strength retention (aging, 72 hours at 125°C)

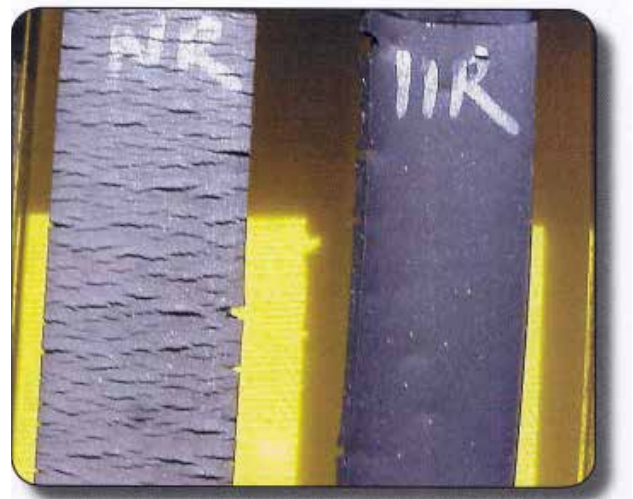


Aging resistance

Oxygen and ozone in the atmosphere will cause natural rubber to oxidize, deteriorate, and eventually crack. Because butyl rubber has good aging resistance, innertubes made from it have a longer life span without the need for additional antioxidant and antiozonants systems. Figure 6 illustrates that unlike natural rubber, butyl rubber innertubes have good aging resistance. In this example both natural rubber and butyl rubber were stretched by 20% and exposed for 72 hours at 40°C and 50 pphm of ozone.

Figure 6

Aging of natural rubber (NR) and butyl rubber (IIR)



Ref: ExxonMobil Company data

Advantages of butyl innertubes to end users (vehicle owners)

In summary, use of butyl rubber innertubes offers a number of advantages to the tire end user such as:

- Consistent inflation pressure.
- Reduction in tire rolling resistance, due to the better inflation pressure retention, which may improve fuel consumption.
- Longer tire life and more even-wear performance.
- Longer innertube life due to better heat stability.
- Enhanced tire durability.

3. Compounding of butyl and chlorobutyl rubber innertubes

The selection of the grade of butyl or chlorobutyl rubber to be used in innertubes is based on service performance requirements and compound processing properties. The choice of other compounding materials is based on manufacturing equipment constraints, cost, local availability and quality of the raw materials. The basic materials for an innertube compound are as follows:

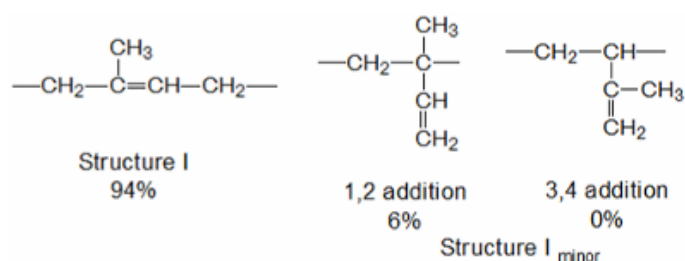
- Butyl rubber or chlorobutyl rubber as the primary polymer,
- Carbon black as the filler,
- Processing aids and Plasticizers,
- Cure system.

Polymer selection

Butyl rubber is a copolymer of isobutylene and approximately 2 mol% isoprene (Figure 1). The length of the isobutylene structural unit (0.270 nm) is 67% of that of the 1-4-isoprene structural unit (0.405 nm)⁷. The stereochemistry of the isobutylene unit results in close packing along the polymer chain, low free volume fraction, and consequently low permeability. Isoprene is incorporated in a *trans*-1,4 enchainment to produce a random, linear copolymer.

Using ¹H NMR to investigate the stereochemistry of the enchainment isoprene, it was found that the majority (94%) of Structure I isoprene units illustrated in Figure 7 are incorporated in the 1,4 configuration⁸. The term 'Structure I', is assigned from the description for isoprenyl units found in chlorobutyl and bromobutyl rubbers.

Figure 7
Stereochemistry of isoprene incorporation⁷



Structure I_{minor} consisting of the 1,2-enchainment isoprene has also been suggested, at amounts in the order of 6%⁸. No 3,4-addition products have been reported. Elaborating on this work, White and coworkers further suggested the absence of a 3,4-addition structure but also suggested that Structure I_{minor} had the configuration illustrated in Figure 8⁹. The ratio of 1,4 enchainment isoprene and the minor isoprenyl derivative was dependent upon polymerization temperature but was still present, albeit in small amounts, in commercial grades of butyl rubber. White and coworkers have also

reported that Structure I_{minor} is not associated with end groups, and that the R groups arise from isobutylene and not from isoprene-isoprene addition. Though the authors indicated no definitive determination of the R-group, evidence was presented showing the R-groups may be longer chains⁹.

Thus, though the presence of a Structure I_{minor} is accepted, its precise configuration remains to be further clarified, the primary difficulty being the very low concentration of such structures.

Figure 8
Proposed structure I_{minor}⁹

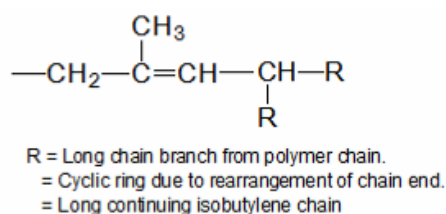


Figure 9 shows the structures of the chlorine containing groups found in chlorobutyl rubber¹⁰. The majority of the isoprenyl units are in the *trans*-configuration. Structure II, the predominant structure in chlorobutyl rubber, represents approximately 60%, followed by Structure I representing 30%. Structure III is not found in chlorobutyl rubber and Structure IV can be up to 10%.

For butyl innertubes, EXXON™ Butyl 268 can be used as a starting point in building a compound formulation. Examples of innertube compound formulations can be found at 'www.butylrubber.com'¹¹. Table IV further illustrates a selection of the commercial grades of butyl rubber and chlorobutyl rubber currently available from ExxonMobil Chemical company. The table shows the range of polymer viscosities available, nominal isoprene content, and in the case of chlorobutyl, the halogen content¹¹.

Figure 9
Possible isoprenyl structures in chlorobutyl rubber¹⁰

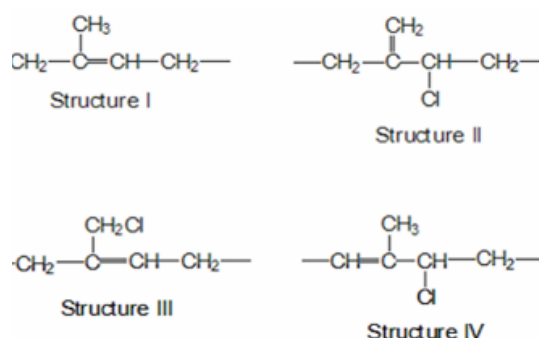


Table IVExamples of commercial grades of ExxonMobil isobutylene based elastomers¹¹

Elastomer	ExxonMobil Grade Identification	Mooney Viscosity (ML1+8 at 125°C)	Isoprene (mol %)	Halogen	Halogen (wt%)
Butyl (low viscosity)	065	32	1.05		
Butyl (medium viscosity)	065 268	51 51	1.05 1.70		
Chlorobutyl	1066	38	1.95	Cl	1.26

Guidelines for innertube compounding EXXON™ butyl 268

The high Mooney viscosity, medium unsaturation polymer EXXON™ Butyl 268, is in many instances a satisfactory selection for innertube applications. EXXON™ Butyl 268 offers a good balance of both processing and performance parameters such as:

- Black and oil incorporation,
- Processing quality (i.e. dispersion, mixing efficiency, extrusion properties),
- Thinning resistance,
- Fold breakdown resistance,
- Cure rate,
- Physical properties such as tensile strength and tear strength,
- Cold buckling resistance,
- Aged physical properties.

In addition, the high mooney viscosity of EXXON™ Butyl 268 in particular also imparts good green strength and fold breakdown resistance to the innertube compounds. The medium unsaturation level of EXXON™ Butyl 268 gives the best balance between adequate cure rate and good aging properties.

Carbon black

Filler addition is a common practice in rubber compounding to (i) reinforce the polymer, (ii) improve compound mechanical properties, (iii) improve compound processing properties by suppressing polymer elasticity, to control die swell, and shrinkage, and, (iv) optimize final compound cost. The proper selection of carbon black is important, because it has a major role in determining the final innertube quality, in addition to the effect on the processing such as mixing, extruding, and vulcanizing.

The effects of carbon black on properties of butyl and halobutyl rubber are similar to that found with other elastomers. As particle size decreases, with a corresponding increase in specific surface area, the tensile strength, 300%

modulus, hardness, viscosity, and damping of carbon black-filled vulcanized rubbers increases. Tensile strength, in general, is raised to a maximum (i.e. critical or optimum loading factor) with carbon black content and then can decrease at higher loading¹². For butyl rubber, the maximum tensile strength is obtained at 50 to 70 phr (part per hundred of rubber) of carbon black depending on the grade:

Carbon black grade	Typical loading
N762	60-70 phr
N660	60-70 phr
N550	50-60 phr

The selection of carbon black in butyl rubber is important in achieving low modulus properties. Low modulus innertubes give better splice strength and flex resistance which is required for radial tube-type tire innertubes.

Low modulus innertube

The concept of “low modulus” innertube compounding is an important parameter for innertubes designed for service in radial ply tires. Radial ply tires have a longer service life than bias ply tires. Moreover, the radial ply construction of such tires results in a higher degree of flexing of both the sidewall and the innertube fitted inside the tire. Thus, not only must the innertube last longer in a radial ply tire, it must do so under conditions that results in a higher stress on the innertube walls and particularly the innertube splice. In this regard, when compared to general purpose rubber innertubes, the advantages of low modulus butyl rubber innertubes could be listed as follows:

- Compound processing:
 - Good flow and green tack, and,
 - Improved splice properties.

- Product service:
 - Low static stress at the splice,
 - Low dynamic stress at the splice,
 - Low stress concentration at the splice,
 - Longer splice durability, and,
 - Flex resistance.

Good splice durability is also required for bicycle innertubes. When compared to automobile tires, the inflation pressure is usually higher. The average inflation pressure in a bicycle tire can be between 60 to 90 psi (5 to 8 bars) which compares with the average inflation pressure of a passenger radial tire of between 25 to 35 psi (1.5 to 2.5 bars). Bicycle tire innertubes generally have thin walls, low surface area for splicing, high surface area to volume ratio, and still must perform satisfactorily at high inflation pressures.

The compound parameter, '100% modulus', is useful in assessing splice durability. The term 'low modulus' indicates a 100% modulus of less than 1.0 MPa which does not increase excessively (less than 50%) after heat ageing for 72h at 125°C. The criteria for low modulus compounds are met by the use of high proportion of larger particle size carbon black such as N660 at about 70phr and paraffinic oil at about 25phr. Such a combination gives good resistance to fold breakdown and facilitates butt splicing. Model formulas for low modulus butyl innertubes, which can be used as a starting point for further compound development work, can be viewed on the website, www.butylrubber.com, under the Formulary section¹¹. Use of non-reinforcing mineral fillers such as calcium carbonate and Kaolin clays in innertube compounds can cause die plating difficulties. In addition to a potential presence of grit or foreign matter, higher rejection and scrap rate caused by pinhole leaks in final innertube may be found.

Processing aids and plasticizers

Processing aids can be subdivided according to both their chemical structure and function. The structure of processing aids

is very diverse and the best classification is by the role played in a compound formulation. The functional role of processing aids includes peptizers, lubricating agents, homogenizing agents, dispersion agents, tackifying resins, plasticizers, and process oils¹².

Process oils

The main requirement for processing aids is to improve compound processability with minimum effect on the final vulcanizate properties. Petroleum based oils are commonly used as plasticizers to lower compound viscosity, improve processability such as shear stress and die swell, and improve low temperature flexibility properties. Plasticizers are selected for their compatibility with isobutylene elastomers and for their low temperature properties. Historically, paraffinic process oils have been preferred in butyl innertubes because of their lower polarity, compatibility, and minimum effect on the state of cure. However, process oils increase air permeability of butyl rubber innertube compounds, whereas increased carbon black loading can lower the permeability. Therefore, the carbon black loading and process oil content should be optimized to accommodate the conflicting requirements of optimum innertube properties and processing parameters. As a generalization, a combination of carbon black (50 to 70 phr) and paraffinic process oil (20 to 25 phr) can be used in butyl innertube compounds. Alternatively, in most climates naphthenic process oils have proven suitable. Aromatic oils may not be suitable for butyl rubber innertubes due to the high polarity and non-compatibility with non-polar butyl rubber. They may also contain relatively high levels of sulfur, some of which may reduce compound scorch resistance and activate the vulcanization reaction. While selecting the compound process oil, avoid oils with high volatility since this can contribute to innertube porosity, which may cause blisters during processing and service. For reference, some properties of process oils are listed in Table V^{12,13}.

Table V

Typical properties of process oils¹³

Physical property	ASTM methods	Paraffinic	Naphthanic	Aromatic
Specific gravity	D1250	0.85 - 0.89	0.91 - 0.94	0.95 - 1.0
Pour point (°F)	D97	0.0 to +10	-40 to +20	+40 to +90
Refractive index	D1747	1.48	1.51	1.55
Aniline point	D611	200 - 26	150 - 210	95.0 - 150.0
API gravity	D287	28.0 - 34.0	19.0 - 28.0	10.0 - 19.0
Molecular weight	D2502	320 - 650	300 - 460	300 - 700
Aromatic content (%)		15.0	44.0	68.0

Note: Aniline point in °C

If low temperature flexibility requirements are more stringent, then this property can be improved by using a blend of low viscosity paraffinic oils and ester-typed plasticizers such as dioctyl sebacate, diisooctyl sebacate, or dioctyl adipate.

Stearic acid

Stearic acid content of approximately 1.0 phr is suggested for butyl rubber innertube compounds as it assists in improving dispersion of fillers. Moreover, stearic acid can act as a release agent and minimize mill sticking during mixing and mold sticking during vulcanization. Stearic acid is also an activator for the cure system and can reduce scorch safety if used in excess.

Poly-p-nitrosobenzene

Poly-p-nitrosobenzene (POLYAC) is used as a heat-treating agent to partially crosslink butyl rubber (by mixing polymer with poly-p-nitrosobenzene for approximately three minutes at 160°C). This may improve butyl rubber green strength. It can be useful where fold breakdown problems occur due to over stacking of green innertubes (between extrusion, splicing and curing), and cannot be addressed by other means. A level of 0.2 to 0.4 phr of this material is adequate. Partial crosslinking of butyl rubber can affect polymer flow during butt splicing and can be detrimental to the splicing operation. The innertube manufacturing industry may therefore take appropriate precautions in using such heat-treating agents so as to monitor any impact on critical innertube splice properties.

Tackifying hydrocarbon resin

Butyl's inherent tack property is lower than that of natural rubber. To improve tack, frequently hydrocarbon tackifying resins are added to assist butt splicing during manufacturing innertubes. Tackifying resin loadings can range from 2.0 phr to 6.0 phr. Melting point of the resin is important for the proper dispersion in rubber. EXXON™ Escorez 1102 (Table VI) has been widely accepted as a good tackifying resin in butyl rubber innertube compound¹⁴.

Table VI

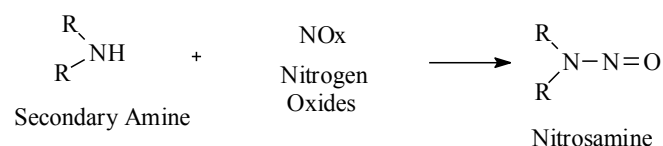
Examples of Escorez™ hydrocarbon tackifying resins¹⁴

Resin	Supplier	Grade	Type	Softening Point (°C)	Melt Viscosity (cps)	Tg (°C)	Mn	Mw
Escorez	Exxon Mobil Chemical	1102	Aliphatic Hydrocarbon Resin	100	7000	50	750	2400
		1304	Aliphatic Hydrocarbon Resin	100	6000	50	750	1650
		1310LC	Aliphatic Hydrocarbon Resin	93	2800	45	750	1350
		1315	Aliphatic Resin	115	5000	65	950	2400

Cure systems

Vulcanization of isobutylene based elastomers introduces chemical cross-links via reactions involving allylic hydrogen or allylic halogen in butyl rubber or halobutyl rubber, respectively. In butyl rubber, the allylic hydrogen atoms positioned relative to the carbon-carbon double bond permit vulcanization or formation of a crosslinked network using sulfur and organic accelerators. The low degree of unsaturation in butyl rubber requires the use of ultra-accelerators, such as thiurams or dithiocarbamates in combination with sulfur, zinc oxide and stearic acid. A secondary accelerator such as 2-mercapto benzothiazole (MBT) or mercaptobenzothiazyl disulfide (MBTS) is also used in typical cure systems for butyl rubber innertube compounds. Cure systems may therefore contain sulfur, zinc oxide, tetramethyl thiuram disulfide (TMTD), MBT, or MBTS, and zinc diethyl dithiocarbamate (ZDEC)¹⁵. ASTM nomenclature for both elastomers and vulcanization accelerators is presented in Appendix 1 and 2 respectively.

In the last twenty years, there has been considerable research directed toward n-nitrosamine formation in thiuram (TMTD) and dithiocarbamates (ZDEC) containing vulcanization systems. Nitrosamines are formed by the reaction between secondary amines released from the rubber curatives and oxides of nitrogen present in air, i.e.:



The formation of nitrosamines is dependent upon the volatility of the secondary amine that is formed due to the participation of the accelerator in vulcanization and its reaction with NOx in the air. Lower molecular weight secondary amines with lower boiling points are more volatile than higher molecular weight molecules. The boiling point of the secondary amine is dependent on the chemical structure of the pendent 'R-groups'. Typically, morpholine containing accelerators, and

with some exceptions, thiurams, and dithiocarbamates generate nitrosamines.

In the formulary section of the website, 'www.butylrubber.com', the butyl rubber innertube compounds are presented with alternative non-n-nitrosamine generating cure systems such as sulfur, zinc dibenzylthiocarbamate (ZBEC) and tetrabenzylthiuram disulfide (TBzTD) as primary accelerators and MBT, MBTS or N-cyclohexyl-2-benzothiazole

sulphenamide (CBS) as secondary accelerators¹¹. Zinc oxide and stearic acid are activators. TBzTD ultimately forms dibenzyl amine (DBA) during vulcanization. DBA has a very high boiling point (300°C) and in the presence of oxygen may degrade before it reaches this temperature¹⁶. Table VII presents some examples of innertube compounds that can be used as starting points for further development work. Abbreviations for accelerators are shown in Appendix 2.

Table VII

Comprehensive comparison of three model innertube compounds

Compound 1. EXXON™ Butyl 268
 2. EXXON™ Butyl 268/Vistalon EPDM 2605 85/15 Blend
 3. EXXON™ Butyl 268, ZBEC/Sulfur Cure System

Material	Test Method Based On	Units and Cond. (2)	1	2	3
Exxon™ Butyl Grade 268	PHR		100.00	85.00	100.00
Vistalon™ EPDM Grade 2605	PHR			15.00	
Carbon Black N660	PHR		70.00	70.00	70.00
Paraffinic Oil	PHR		25.00	25.00	25.00
Exxon Escorez™ Resin Grade 1102	PHR		4.00	3.00	3.00
Stearic Acid	PHR		1.00	1.00	1.00
Zinc Oxide	PHR		5.00	5.00	5.00
Mercaptobenzothiazyl disulfide (MBT S)	PHR			1.00	
Zinc Dibenzothiazylthiocarbamate (ZBEC)	PHR				1.50
2-Mercaptobenzo thiazole (MBT)	PHR		1.00		
1,3-Dibutylthiourea (DBTU)	PHR		2.00	2.00	
Sulfur	PHR		2.00	2.00	2.00

Properties	Test Method Based On	Units and Cond. (2)	Typical Values		
Mooney Viscosity, ML 1+4	ASTM D 1646	MU at 100°C	42.6	46.1	43.5
Mooney Scorch	ASTM D 1646	at 125°C			
Minimum Viscosity		MU	31,9	34,3	
Time to 5pt rise		minutes	14.1	13.1	21.8
Time to 10pt rise		minutes	18.7	17,7	25.9
Rheometer (ODR)	ASTM D2048	160°C, 60 min., 3.0 deg.arc			
Mi (Minimum torque)		d<nm	8	8.6	6.6
Mh (Minimum torque)		dNm	47.2	54.9	54.8
Mh - Mi (Delta torque)		dNm	39.3	46.3	48.2
T s2 (time to 2 point rise)		Minutes	2.3	2	4.1
T c50 (time to 50% torque increase)		Minutes	14.6	14.4	
T c90 (time to 90% torque increase)		Minutes	42.7	43.3	37

Properties	Test Method Based On	Units and Cond. (2)	Typical Values		
Rheometer (ODR)	ASTM D2048	180°C, 30 min., 3.0 deg.arc			
Mi (Minimum torque)		d<nm	8	8	5.8
Mh (Minimum torque)		dNm	51.1	51.1	44.7
Mh - Mi (Delta torque)		dNm	43.2	43.2	38.9
T s2 (time to 2 point rise)		Minutes	4	4	1.8
T c50 (time to 50% torque increase)		Minutes	4	12.4	
T c90 (time to 90% torque increase)		Minutes	11	12.4	7.2
Rheometer (ODR)	ASTM D2048	160°C, 60 min., 0.5 deg.arc			
Mi (Minimum torque)		d<nm	1.4	1.5	1.3
Mh (Minimum torque)		dNm	9.5	11.1	10.6
Mh - Mi (Delta torque)		dNm	8.1	9.6	9.3
T c50 (time to 50% torque increase)		Minutes	12.1	11.6	
T c90 (time to 90% torque increase)		Minutes	40	40.4	23
Rheometer (ODR)	ASTM D2048	180°C, 30 min., 0.5 deg.arc			
Mi (Minimum torque)		d<nm	1.3	1.3	1.3
Mh (Maximum torque)		dNm	8.6	10.3	9.5
Mh - Mi (Delta torque)		dNm	7.3	9	8.4
T c50 (time to 50% torque increase)		Minutes	2.7	2.8	
T c90 (time to 90% torque increase)		Minutes	8.9	10	5.6
T en sile Strenght		MPa	11.2	11.3	9.9
Elongation at Break		%	775	760	630
Modulus 100%		MPa	0.9	1.1	1.5
Modulus 200%		MPa	1.7	2.1	
Modulus 300%		MPa	2.6	3.2	4.3
Energy te Break		Joules	9.8	10.1	8.2
Tear Strenght (Die B) Mean		KN/m	30.8	26.8	17.8
Tear Strenght (Die C) Mean		KN/m	31.4	33.5	27.4
Hardness		Shore A	54	57	54
Rheometer (ODR)	ASTM D412	Aged 125 deg C, 72 hours			
T en sile Strenght		MPa	8.2	7.9	7.1
Elongation at Break		%	58.5	49.5	57.0
Modulus 100%		MPa	1.5	1.8	1.3
Modulus 200%		MPa	3	3.7	
Modulus 300%		MPa	4.4	5.4	3.9
Energy te Break		Joules	7.2	6.1	5.9
Tear Strenght (Die B) Mean	ASTM D624	KN/m	22.8	22.1	21.8
Tear Strenght (Die C) Mean	ASTM D624	KN/m	27.2	24.8	25.2
De'Mattia Flex Resistance	ExxonMobile Method	Kilocycles KC	>80 No Cracks	>200 No Cracks	

Notes: 1. PHR: parts per hundred rubbers. 2. Values given are typical and should not be interpreted as a specification.

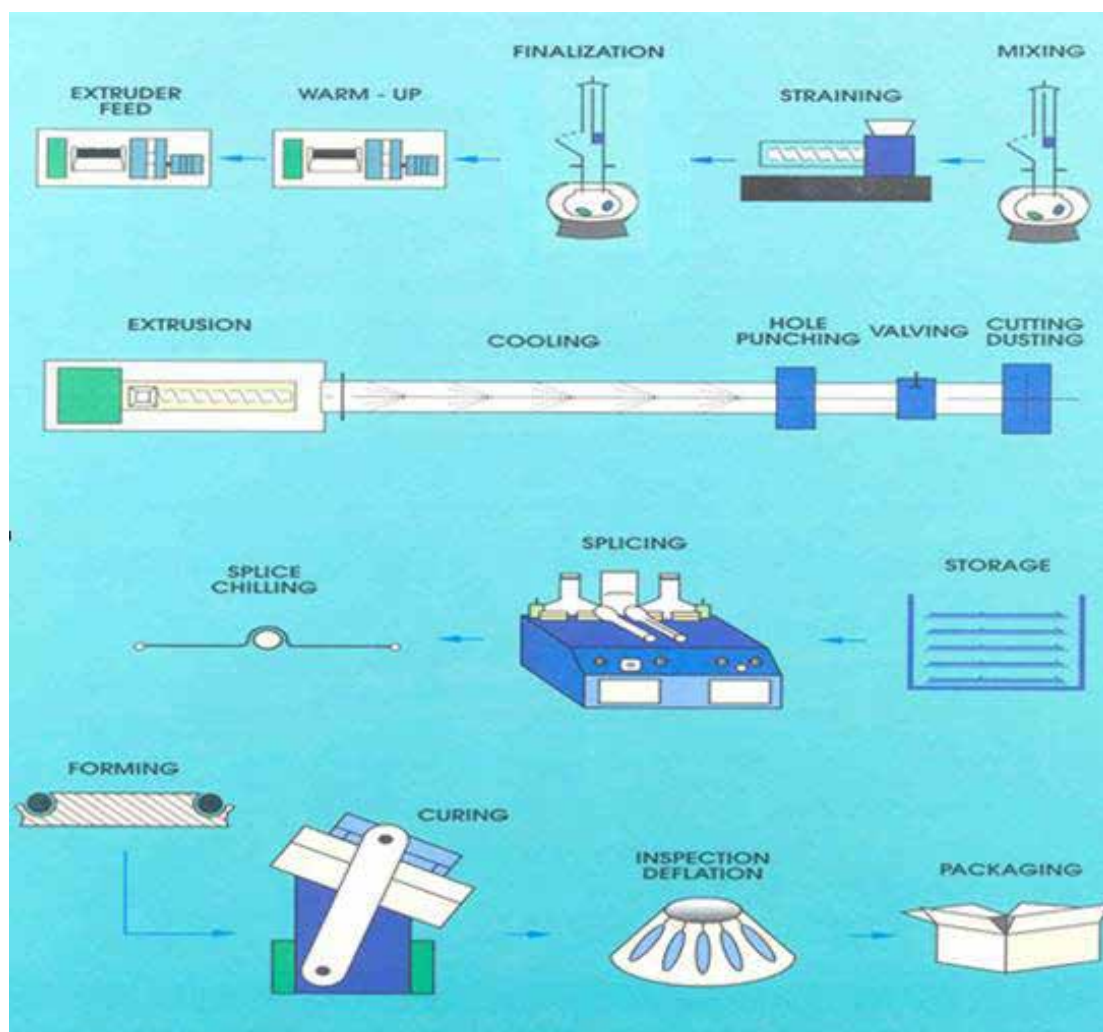
4. Processing of butyl rubber innertube compounds

Manufacturing process sequence

The processing of the butyl rubber innertube compounds and the manufacture of the innertubes involves mixing the compound masterbatch, or non-productive, and final batch or productive, straining, extrusion, cooling, dusting, and finally cutting to length. Depending on the production facility, this is followed by various additional steps such as valve fitting, splicing, splice chilling, forming, vulcanization, inspection and deflation, and final packaging. A schematic of a typical butyl rubber innertube manufacturing process is illustrated in Figure 10.

Figure 10

Schematic of a typical innertube manufacturing process



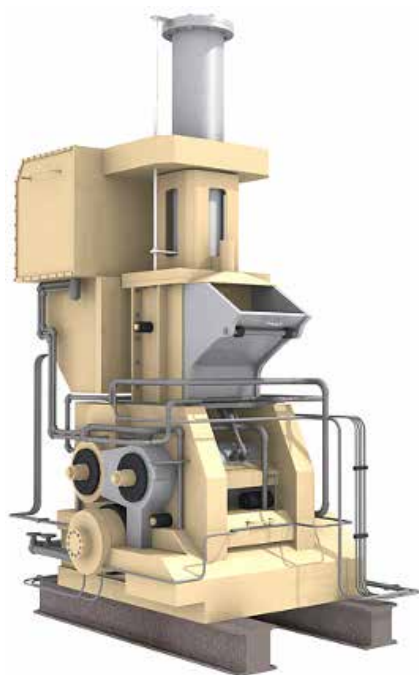
Guidelines for mixing

Because butyl rubber is primarily a saturated polyisobutylene polymer with only a minor quantity of isoprene, it is important that contamination of butyl rubber stocks with highly unsaturated elastomers such as natural rubber, SBR, and cis-polybutadiene rubber be avoided. Contamination results in a difference in the state of cure for butyl rubber compared to other unsaturated diene rubbers resulting in variability and potential loss of mechanical properties. Internal mixers, two roll mills, strainers and extruders used for processing both butyl rubber and unsaturated rubber compounds should be cleaned thoroughly before mixing and processing of butyl rubber compounds. To do this, a clean-out masterbatch of the type of compound to be processed next may be passed through the equipment. After this step, a visual inspection may be made to determine if there is no compound remaining in the equipment. These two steps are typically sufficient to avoid most cases of contamination.

Masterbatch mixing

Masterbatch mixing of butyl rubber innertube compounds is typically carried out in an internal mixer (Figure 11). Finalization (i.e. addition of the vulcanization system) may be carried out separately in an internal mixer, on open mills, or sometimes in a single stage masterbatch mixing/final batch mixing cycle.

Figure 11
Internal mixer



The mixing of the butyl rubber innertube masterbatch compound is an important operation in the innertube production process. The objective is to disperse the carbon

black and other materials in the butyl rubber uniformly with no porosity in the final compound. Poor mixing may have a detrimental effect during later stages of processing such as:

- Strainer screen plugging,
- Variability in extruded innertube dimensions (gauge uniformity),
- Fold breakdown,
- Difficulty in splicing, and,
- Uneven thinning during forming, or gauge retention.

The objective for mixing ideally is “the first time right” approach. When a mixed compound contains imperfections, it may be very difficult to make corrections to the compound. To achieve good dispersion of the compound, the following parameters are important:

- Compound formulation,
- Mixer volume loading,
- Initial mix temperature,
- Timing of black and oil addition,
- Order of addition of other compounding ingredients, and,
- Compound mixing dump temperature.

Guidelines for mixing of butyl compounds

Representative model innertube compounds are shown in www.butylrubber.com under the formulary section¹¹. Hot housing of halobutyl and butyl rubber up to 40°C will help in mixing of these materials. However, time in a hot house should be kept to a minimum and should not exceed 72 hours. Good air circulation around the bales of rubber and around the pallets is essential¹⁰.

Internal mixer volume loading

The optimum loading for an internal mixer for general purpose rubbers is defined as the empty volume multiplied by the fill factor. The empty volume is the volume of liquid it would take to fill the mixing chamber. Fill factors are normally in the range 0.7 to 0.8 depending on mixer size and design. Since butyl rubber innertube compounds are softer, it is necessary to increase the batch size by 10 to 15% above the normally recommended level. Higher loading of butyl rubber compounds enhances the mixing quality and reduces the chances of air trapped in the compound which is an important step in minimizing porosity in the finished innertube. Defects in butyl rubber compounds related to trapped air can increase processing and cured innertube scrap. Once air gets into butyl rubber compounds it cannot escape easily. Thus, the batch size for a butyl rubber innertube compound is calculated differently:

- Example: 11D Banbury mixer
- Empty volume: 34 litres
- Fill factor: Butyl rubber non-productive = 0.80 - 0.85
- Butyl rubber productive = 0.75 - 0.80
- Typical specific gravity = 1.135
- Batch volume: $234 \times 0.8 = 187$ litres
- Batch weight: $234 \times 0.8 \times 1.135 = (187 \times \text{S.G}) \text{ kg} = 212 \text{ kg}$

Optimum loading will also depend on the state of wear of the mixer (e.g. mixer rotor flight clearance). The above formula may be used as a guide to calculate a batch weight starting point. An alternative starting point guide is to use 12% greater loading than that used for a SBR or NR compound of equal specific gravity. By mixing a series of batches, where batch weight is increased in 5 kg increments, and number of imperfections in each batch is assessed the best mixer loadings and run conditions may be determined.

Internal mixer starting temperature

A temperature of around 90°C is a suggested compromise between cycle time and mixing quality. To maximize mixing uniformly, consistency in time between consecutive batches is suggested.

Time of carbon black addition

It has often been considered that carbon black addition to a conventional butyl mixing cycle can occur quite early as the polymer does not undergo peptization during mixing. However, a degree of mastication of the butyl rubber converts the initial rough lumps into a continuous mass, which more readily accepts black. This is particularly true in colder climates where undispersed polymer lumps may be more prevalent. Typically, the first part of carbon black addition is made after approximately 30 seconds of rubber mastication.

Order of another ingredient addition

Zinc oxide and stearic acid are generally not added with the polymer as they could create a coating, reduce shear, and adversely affect mix quality. If the carbon black addition is split, zinc oxide may be added with the first addition of carbon black or with stearic acid during the subsequent remaining carbon black and oil addition. Process oils, if added with the first addition of carbon black, may reduce viscosity and shear. The oils may alternatively be added with the last part of carbon black addition.

Dump temperature

Compound dump or drop temperatures of 145°C to 155°C are suggested for the non-productive to obtain optimum mix quality. Some internal mixers may give adequate mixing at lower dump temperatures. However, where promoters are used, higher temperatures may be important to ensure complete chemical reaction. Dump temperatures should

always exceed 125°C to ensure melting and dispersion of the bale wrap film used on butyl rubber bales.

To further aid in preventing contamination, all stocks should be labeled prominently and carefully segregated to avoid accidental contamination. The use of distinctively colored stock markings, batch cards, segregated stock bins and racks have all been found helpful in this regard. An important factor is also training of factory personnel on the importance of factory stock handling procedures.

Guidelines for mixing cycle

Table VIII shows two conventional mixes cycles. Normally, good results can be achieved by polymer mastication and one carbon black addition Table VIII A). Mixing cycle time is dependent on the condition, capacity, and design features of the internal mixer.

Table VIII

A. Conventional method of master batch

Mix time/drop (dump) temperature	Material or action
0	Add polymer
30 seconds	Add carbon black, zinc oxide
130°C	Add oil, stearic acid
140°C	Clean ram
155°C	Dump on mill for sheeting

B. Alternate simplified method of mixing

Mix time/drop (dump) temperature	Material or action
0	Polymer
30 seconds	2/3 rd carbon black, zinc oxide
3 minutes	1/3 rd carbon black, oil, stearic acid
4.5 minutes	Clean ram
155°C	Dump on mill for sheeting

Guidelines on alternative mix procedures

Two additional mix cycles are of interest here, an "upside down mixing" and mill mixing.

- *Upside-down mixing*: the upside down mixing cycle (Table IX) requires the mixer to be in excellent condition (i.e. temperature control, rotor condition, seals, pressure control,

etc). Mix quality may not be comparable to that obtained with conventional mixing cycles. However, it is generally satisfactory with medium particle size carbon black (FEF, GPF, SRF), but is less effective with fine particles blacks such as N330 (HAF). The principal advantage is potential reduction in cycle mix times.

Table IX

Alternate mixing cycle (upside down mixing)

Time (minutes) & dump temperature	Material or action
0	Carbon black, zinc oxide, oil, stearic acid, polymer (in this order).
4 minutes	Clean ram
155°C	Dump on mill for sheeting

- *Mill mixing:* as mentioned earlier, masterbatch mixing of butyl rubber innertube compounds is typically carried out in an internal mixer. Butyl rubber does not break down on milling and the uncompounded polymer has a tendency to crumble if high mill speeds or wide mill roll openings are used. After incorporation of about 10 phr of carbon black, butyl rubber behaves relatively smoothly on the mill and readily accepts additional pigment or oil. Thus, special techniques such as adding the first 10 phr of carbon black at the beginning of the butyl rubber compound mixing can be very useful. Without these techniques, the mill mixing of butyl rubber may be difficult.

The best way to avoid crumbling during the early part of mixing is to leave a small portion of the previous batch on one side of the mill. The first butyl bale of the new batch is added to this "leader". The "leader" compound and fresh rubber are allowed to mix in the mill nip without cutting. A blend containing about 10 phr of black will thus be obtained and mixing may then proceed.

If no "leader" is available, the first 10 phr of black should be added to a small portion of the polymer on one side of a tight mill. Initial mill roll temperatures of 35°C to 55°C are suggested. If stearic acid is used, it should be added at the beginning of the mix. As soon as sufficient pigment is added to obtain a smooth band of polymer on the mill, the mill may be opened and the same procedure followed as with a "leader" compound.

During milling, butyl rubber tends to go to the cooler side of the mill rolls. If the stock "bags" or goes to the (faster) back roll, the back roll should be kept warmer than the front roll. A

temperature differential of 10°C is usually sufficient to keep the stock on the front roll.

Guidelines for straining

Butyl rubber innertube compounds can be strained for foreign material, undispersed carbon black particles, or other contaminants. The masterbatch is best strained immediately after mixing to eliminate an extra warm-up operation if suitable capacity straining equipment is available. This can be done by strip feeding the strainer from the batch-off mill or feeding directly into a batch-off extruder and strainer.

Equipment is available which will handle the dumped stock within the duration of the mixing cycle. If the treatment is not possible the more common operation of a separate mill warm-up of the stock is usually adopted. Strainer packs are usually 30 mesh or 20 mesh backed up by 40 mesh. Table X shows potential maximum particle dimensions obtained after passing through various screens of different mesh sizes.

Table X

Mesh size¹⁷

Mesh Size	Dimensions
10	2.00 mm
20	850 µm
30	600 µm
40	425 µm
60	250 µm
80	180 µm

Efficient cooling and minimal heat history are prerequisites for straining finalized compounds. Strained finalized compound may go directly to the extruder.

Often, straining of finalized stock by a screen pack in the extruder is practiced. The compound must be particularly well mixed and high-quality curatives used to minimize screen changing. However, this process may not be suited to good tube dimensional control due to output rate changes as the screen becomes plugged. A double head extruder is advantageous to minimize time lost during screen changes.

Guidelines for final batch mixing

Curatives may be added to butyl rubber innertube compounds by various methods, (i) on the extrusion warm-up mill prior to extrusion, (ii) in a short mix time, low temperature, internal mixer cycle (drop temperature 100°C to 105°C), (iii) or by a one-pass internal mixer mixing method. In the last two methods, straining of the finalized compound is suggested due

to the possibility of contamination by small, often wholly or partially cured lumps left in the mixer from previous batches. If the curatives are added on the warm-up mill, a second feed mill for the extruder is useful to ensure complete dispersion of curatives before feeding to the extruder. Before finalizing, the master batch is frequently stored for a minimum of two hours, or preferably for a full shift, to allow cooling and stock relaxation. This allows maximum rubber-carbon black interaction, which improves green strength.

Guidelines for extrusion

While hot feed extrusion is a widely practiced technique, cold feed extrusion is used in some newer plants. In either case, an innertube of uniform dimensions with minimum porosity is the objective.

Hot feed extrusion

- Hot feed extrusion guidelines can be summarized as follows:
 - Care should be taken to assure an adequate supply of compound to the mills, prevent porosity, and maintain the uniform compound temperature. A small rolling bank should be maintained on the feed mills.
 - The mills should not to be overloaded and compound dwell times controlled.
 - Slight excess of stock is suggested in the extruder feed box to ensure that the screw flights are full, thereby preventing an excessive intake of air with the compound feed strips.
 - A force feed roller which will ensure the effective filling of the screw flight at the feed end is useful but the occasional addition of some extra strips of compound to the hopper may also be advantageous.
- Temperature control:
 - Feed strip temperature of between 80°C to 90°C at the mill is suggested.
 - Extruder die temperatures of 110°C to 120°C are, again, suggested.
 - Barrel and screw suggested temperatures should be between 50°C to 60°C with the screw cooler than the barrel.
- Take-off conveyor:
 - Speed of the take-off conveyor should match the extrusion speed.
 - Pull-down should be avoided as it may result in increased innertube wall porosity and uneven shrinkage on cooling.
 - The crown gauge, which undergoes thinning in the forming operation, is usually extruded at 1.5 to 1.6 times the thickness of the base.

Cold feed extrusion

Cold feed extrusion may also be used for the production of the

innertubes. The higher back pressure and the vacuum venting facility of most cold feed extruders assist in the removal of air and moisture vapor which allows for a low porosity extrudate to be produced. For best results, the feed strip should have uniform viscosity. Therefore, the compound should be well mixed and multiple batches blended prior to strip preparation. A one-step straining and extrusion process, with a quick-change device for screen replacement, is suggested for improvement in productivity. Gauge reduction is possible with cold feed extrusion due to the ability to produce a lower porosity extrudate.

Dusting of innertube interior

Talc, or other dusting agents such as starch, is blown into the interior of the innertube during extrusion to prevent the collapsed innertube from adhering to itself. Zinc stearate may be used but it has to be a grade of sufficiently high melting point to prevent fluxing in the innertube interior during extrusion.

Identification of butyl innertube

The application of a blue line (Table XI) to the butyl innertube during extrusion is useful. It enables the splice to be detected easily for cured innertube inspection and identifies the innertube as butyl rubber to reclaim rubber processors. The light thin blue line should be applied so that it dries before entering the cooling zone.

Table XI

Blue line compound	
Exxon Butyl 268	100.00
Calcium Carbonate (Whiting)	70.00
Titanium Dioxide	20.00
Monastral Blue	As Required
Zinc Oxide	5.00
DBTU	2.00
MBT	1.00
Sulphur	2.00

20% solids in solvent, hexane

Cooling of innertube extrudate

Butyl rubber innertubes should be well cooled after extrusion by passing through a cold-water spray or immersion system in a synchronized cooling line. It is particularly important that the folds are well cooled, especially truck, tractor, and OTR tire innertubes. Warm folds are particularly susceptible to fold breakdown. All water should be blown off the surface of the innertubes after leaving the cooling section.

Application of polyethylene patch

A polyethylene patch is applied to the cooled innertube in the area where the valve will be placed. The patch may be applied before cooling but this may cause wrinkling. The polyethylene should have a smooth surface, a size of approximately 10 cm x 10 cm, and a gauge of approximately 0.1 mm is suggested. It should be brightly colored, so that it is readily visible on the innertubes. Valving of innertubes may also be carried out on-line. The innertube is then dusted or dip coated externally with talc, zinc stearate or other suitable release agent after application of logo and labels with size and other technical information. Innertubes are then cut to length and usually passed to storage in "bear trap" racks or "spring leaf trucks/racks" (Figure 12).

If possible, the green innertubes should not be stacked one on top of the other, as this may result in fold breakdown. The innertubes are preferably stored for the duration of one shift, which will ensure good condition for splicing.

Guidelines for recycling of compound

Materials for recycling must be free of water and extraneous materials such as valve patches and valves. Thus, care must be taken to exclude water at all possible points of entry. Lengths of extruded innertube with open ends should have the ends folded over if they are passed through a cooling section and any holes in the innertubes should be pulled together and sealed. Water, together with dusting agents and polyethylene patches, can be potential sources of blisters and porosity in cured innertubes.

In the manufacture of butyl rubber innertubes, a certain amount of uncured compound may be recycled. The most common source of recycled material is extruded innertubes which are out-of-specification for dimensions, have uncured splice faults, and occasionally, uncured innertubes which have been damaged during storage. If there is no scorched material or other foreign matter in the rubber, this material can be blended in at up to 10% for passenger tire innertubes and up to 20% in truck and larger tire innertubes. For hot feed extrusion systems, it should be added at a uniform rate on the warm-up mill. In this way, no detrimental effects on dimensions are observed. Recycling may reduce the scorch safety of a new compound.

Figure 12

Spring leaf trucks for storage of extruded innertubes



5. Manufacture of butyl rubber innertubes

Guidelines for valve installation

Butyl rubber innertubes should be fitted with butyl rubber valves that meet the tire standards of various countries such as the Tire & Rim Association of United States of America, European Tyre and Rim Technical Organization (ETRTO), Japan Automobile Tire Manufacturing Association (JATMA), International Standard Organization (ISO), Chinese National Standard, or Indian Tire Technical Advisory Committee (ITTAC). Innertube valve quality is very important for air pressure retention. An example of a butyl rubber base valve is shown in Figure 13.

Figure 13

Tube valve schematic



Valve application is sometimes made after cooling on the extrusion line but more commonly immediately before or after splicing. On-line valve application is usually restricted to passenger car or smaller innertubes. Pad edge lifting often occurs with this technique due to the shrinkage of the uncured innertube during storage. Valving after the splicing operation has a number of advantages:

- It allows the innertube to be spliced, crown down, if required, which gives improved splicing on some types of machine.
- Minimizes the possibility of valve dislocation at the splicing or earlier installation stages.
- Reduces the chances of damage to other innertubes.
- Allows recycling of off-specification innertubes without the additional labor of valve removal. The valve hole can be punched before splicing.

Valve cements are often made from a regular innertube compound containing additional tackifying resin (typically a phenol formaldehyde resin), and vulcanizates with 1 to 2 phr of the accelerator, DBTU and MBT, and then dissolved to 10 to 15% solids in a suitable solvent (e.g. 90% hexane 10% MEK). Though such compounds may be sufficient, it might be inadequate under more severe conditions of hot climates where cement with higher green strength may be necessary.

Higher green strength could be achieved by adding 30 to 40 phr of carbon black, without oil, and around 20 phr of a phenolic tackifying resin commonly used in tire compounds.

The valve cement is applied to the base of the valve pad, which has been previously buffed to a smooth, fine edge. A thin single coat of well-compounded cement is suggested. Sufficient drying time to allow all solvent to evaporate from the adhesive is required (generally 2 hr at 50°C). The cemented pads must be protected from dust, dirt, and talc. It is not normally necessary to apply adhesive to an innertube, which has been protected by a polyethylene patch. In the case of online valving, an automatic freshening of the innertube in the valve area, followed by passing it under an infra-red lamp to dry off solvent, may be advantageous.

Butyl rubber innertube valves should be applied to the innertube with a soft (45 Shore A) rubber foot shaped to cover the valve and pressed against the innertube by a pneumatic piston for 4 to 5 seconds. This pressure application allows the butyl rubber compound time to flow sufficiently to ensure a good contact. The technique of using a steel-footed tool struck by a mallet or hammer, sometimes used with GPR innertubes, may not be as effective.

Guidelines for splicing

Splicing, like mixing, is an important step in butyl rubber innertube production and should be performed as efficiently as possible, since splice faults often form a large proportion of total rejects. The worldwide trend of increasing use of radial ply tires has meant that greater performance demands have been made upon the innertube splice which must withstand the higher degree of flexing of the radial tire sidewall and the innerliner splice must continue to do so throughout the much longer life of a radial tire.

Butyl rubber innertubes are spliced by a number of techniques. Fully automated butt splicing machines may be employed, requiring only the placing of the innertube ends in the clamps of the machine and activating the 'start' to perform the operation. Alternately a manual butt splice, consolidated by mechanical means (weld stitch) or a manual lap (overlap or telescopic) may be used.

Most automatic or semi-automatic butt splicing machines have the following mode of operation. The ends of the innertube to be spliced are cut to length by a hot knife and the fresh tacky surfaces are butted together and consolidated. Equipment for this operation can be classified by two important features: (i) vertical

or horizontal cutting mode, and, (ii) solid metal or rubber-faced clamps. Earlier designs of machines had vertical cutting knives and solid jaws. Satisfactory butt splice quality was obtained with a horizontal cut and rubber-faced clamps. These features are integrated into the Exxon Chemical Universal Innertube Splicing Machine (ECUISM) and other newer machine designs¹⁷.

Vertical cut, laminated steel clamp innertube splice machine

These machines were introduced before the advent of the radial tire and will produce splices which are satisfactory for bias ply tires. They can also be used to splice innertubes intended for radial ply tires. However, an easy splicing, low modulus, compound must be used and close attention to the setting and maintenance of the machine is necessary. If this is not done, splices of lower quality may result. The production of good splices in butyl rubber innertubes is strongly influenced by proper adjustment of the machine. It is suggested that the machine adjustments be checked at frequent intervals, as well as at the beginning of a shift, or when a size change is made. Settings such as anvil position, overhang, knife temperature, splicing time, and pressure should be checked at these times. These machines are also commonly used for splicing bicycle innertubes.

Horizontal cut, rubber faced clamp machine (ExxonMobil Chemical Universal Innertube Splicing Machine (ECUISM))

This is a versatile type of machine, which will produce a good quality innertube splice, and which is suitable for use in radial ply tires¹⁸. There are many manufacturers and suppliers of this equipment worldwide. This type of splicing machine is illustrated in Figure 14. Three sizes of machine are available which will cover flat widths from 100 to 600 mm. A few suppliers offer adaptors to cover widths below 100 mm. In addition, where jaw widths are continuously adjustable, the machine can be useful in handling a continuously changing spectrum of sizes.

Figure 14
Innertube splicing machine



The general features described in this section are common to most machines but detailed design difference exists, such as internal or external hydraulic systems, electrically powered ball or screw drivers, and hydraulic actuation system for the knives.

Machine details and operation guidelines are generally given by the splicing machine suppliers (Appendix 3). The major parts and features of the ECUISM splicing machines are:

- *Knives*: features include:
 - Horizontal cut mechanisms.
 - Programming for temperature and speed.
 - Long life alloys, materials, largely self-cleaning when processing butyl rubber innertubes.
- *Clamps*: features include:
 - Universal hydraulic actuation, with rubber clamp faces.
 - Accepts most common passenger and truck innertube sizes. Tractor and off-the road innertubes can be processed on some machines.
 - Easy size change.
 - Fine adjustment for minor flat width variations.
 - Automatic gauge compensation.
 - Reinforced splicing.
- *Butting table*: features include:
 - Hydraulic actuation with very high butting forces.
 - Two speeds with a slowdown at final closing and initial opening movements.
- *Safety*: features include:
 - Twin starter buttons requiring two hand operation.
 - Clamps lift if the starter buttons are released before they have completely descended.
 - Kick bar immediately lifts clamps and opens table or lifts clamps and stops knife, according to which part of cycle is in progress.
 - Guarded clamp covers table opening on many machines.
- *Operation sequence*: the operating sequence can be summarized in a series of points as follows.
 - Innertube inserted: start buttons pressed.
 - Clamp arms descend rapidly, then slow down on final approach to prevent innertube damage, low pressure applied.
 - Knife, at low heat, approaches rapidly from rear of the machine.
 - Knife slows down before entering rear fold.
 - Switch on high heat.
 - Knife enters innertube.
 - Engage cutting speed.
 - Knife drops to low speed just before front fold.
 - Switch from high heat to low heat.
 - Knife leaves front fold.
 - Knife returns to rear of machine at high speed.
 - High clamping pressure applied just before butting.
 - Table closes, initially fast with slow down over final travel; innertube faces deform allowing gauge increase for splice reinforcement.
 - Butting pressure applied for preset dwell time.
 - Table opens, slowly at first, then more rapidly and then lifts clamp arms.
 - Remove innertube for inspection of splice quality.

Machine set-up for splicing-function of controls

Permanent adjustments are those which, for a given innertube compound, are not changed with a change in innertube dimensions. Running adjustments are those which may need to be done with innertube size changes.

1. Safety

Good safety practice suggests that no more than one person at a time can use or adjust the machine. On some occasions, two mechanics may be required to adjust the machine. In this case, one person must not operate the machine without first initiating appropriate warnings.

2. Permanent adjustments

Permanent adjustments are made to:

- Knife current variance (high heat and low heat).
- The clearance between the knives and the rubber faces.
- The cutting angle of the knives.
- The alignment of the rubber faces.
- Knife slowdown points.
- Knife low speed duration time.
- Table slowdown point.

3. Knife current variance (high and low heat)

The knife is kept at a low heat in the rest position, during the approach and on return to the rear of the machine. High heat is used during the cut. Typical values for butyl rubber innertubes are:

- Low heat: 25-30 amps
- High heat: 55-65 amps

Guidelines on typical starting condition for universal innertube splicer are shown in the Table XII.

Table XII

Guidelines for starting conditions for butyl innertube (universal innertube splicers)				
Flat width	Cm	12-20 cm	20-25 cm	25-34 cm
Knives settings	Amp	25-30	25-30	25-30
Low heat current	Amp	55-65	55-65	55-65
High heat current	Second	1.5-1.0	1.0-0.75	0.5
High heat transition	Second	1 cm before fold	1 cm before fold	1 cm before fold
High-low speed transition	Second	1	1	1
Low speed transition	Second	0.5	0.5	0.5
Cutting low speed transition	MPa (psi)	2.0-2.5 (300-360)	2.5-6.3 (360-430)	3.5-4.0 (500-570)
Clamping pressure:/Low (cutting)	MPa (psi)	5.0-6.4 (640-910)	5.0-8.0 (850-1100)	8.0-10.0 (1100-1470)
High (butting)/Butting pressure	MPa (psi)	5.0-6.4 (640-910)	5.0-8.0 (850-1100)	8.0-10.0 (1100-1470)
Butting time	Second	4-7	6-9	8-12

4. Clearance between the rubber faces and the knives

The clearance between the rubber faces and the knife controls the overhang after the cut. This gap can be adjusted to 1.0 mm to 1.2 mm. Excessive overhang can result in rind formation, resulting in insufficient compound in the splice and potentially allowing a separation.

Rind can also refer to the formation of a hump at the splice which can be buffed off, flash which can be shaved off, or lace strips at the splice which can be readily pulled or peeled off. Unequal overhang may cause rind, as well as misalignment, or splice openings.

5. Knife cutting angle

The knife angle is normally $11^{\circ} \pm 1^{\circ}$ to the plane of the cut. However, the machine manufacturer's specifications should be consulted for the actual setup. The machine setup can also be checked by the careful use of a protractor or by the use of a suitable jig from a factory workshop. Cutting angles greater than 12° can result in a wavy cut while cutting angles less than 10° can cause smearing.

6. Alignment of rubber faces

Hardness of the rubber jaw faces for ECUISM type splicers should be approximately 60 Shore A. Compounds based on passenger tire treads, containing N330 carbon black, may be suitable for this application. The rubber clamp faces are to be aligned horizontally and vertically to eliminate the possibility of a stepped splice. A test splice can be made with short pieces of innertube. The splice can be opened after first marking the entry fold, and examined for step-off or misalignment.

If misalignment is evident, the clamps can be shimmed so that the step-off is eliminated. The table approach slowdown must be properly adjusted before this test. Absence of slowdown may cause a step, rolling, or splice hump even when the jaws are properly aligned.

7. Knife slow down points

These are usually selected by moveable slotted fingers on the knife carriage, which operate appropriate magnetic induction proximity switches. They are moved backwards or forwards to adjust the slow down points which can be 1.0-1.5 cm before the fold entry or exit points. The upper finger usually adjusts entry slowdown.

8. Knife low speed duration timer

The timer controls the duration of knife slow speed after the initial transition before entering the rear fold. Normally it is set so that the slow speed is engaged for 1-1.25 cm after entry.

9. High-low heat transition timer

Control of the transition of current in the knife, from high to low prior to the exit fold is the function of the timer. A setting of 0.5 seconds is typical.

10. Running adjustments

The running adjustments to the machine when in operation include:

- Clamp width (flat innertube width)
- Clamping pressure
- Butting pressure
- Butting time
- High heat initiation point

Table XII gives guidelines on starting conditions for butyl rubber innertubes, divided into three groups according to flat width. These settings should only be viewed as a guide since setup conditions may vary from factory to factory. The compound type, age of the stock, porosity level, profile uniformity, and ambient temperature can all influence the conditions necessary to achieve good splices. It should be noted that the machine could typically take about thirty minutes to reach operational uniformity.

11. Butting time

Butting time should be minimum possible to ensure splice quality and minimize fold breakdown in the splice area.

12. High heat initiation timer

This can be set to initiate the high heat about 1 cm before entry fold. The 'switch on' point can be estimated by observing the knife movement and the ammeter. If the initiation is too early, the cut end may be scorched at the entry fold (shiny appearance) and will open during subsequent handling. If initiation is too late, the entry fold cut edge may be smeared and the splice may again be weakened at the entry fold.

13. Tuning the machine set-up

The following points regarding machine control settings should be monitored to assist in achieving the desired output.

- Ensure that knife entry and cutting speeds are at the maximum level. These speeds can be varied on many machines. Note that truck innertubes often accept higher cutting speed than passenger innertubes.
- Adjust the knife high-slow speed transition as close to the entry fold as possible, and, likewise the cutting slow speed transition at the exit fold.
- Minimize the duration of the low speed at the entry fold consistent with splice quality.
- Adjust clamp descent slowdown as late as possible without

permitting the clamps to meet at the high speed.

- Set the table approach slowdown as late as possible without permitting the clamps to meet at high speed.
- Check if one or two seconds can be reduced in the butting time by splicing, curing and checking a few innertubes. With some compounds, increasing butting pressure may compensate for reduced butting time.

Careful attention to these points can sometimes reduce the total machine cycle time by up to 5 to 10%, with a corresponding output improvement.

14. Splice quality criteria

An uncured splice made on a well-adjusted universal splicing machine shows the following properties:

- Well consolidated fold region, internally and externally with minimal distortion and breakdown.
- Good overall alignment, internal and external (i.e. no stepping)
- No rind tails (flash) or cracks.
- If a 2.0 cm wide splice section is gripped with the fingers about 1.5 cm from the splice and elongated 25% for 2 minutes; the sample should stretch uniformly without undue thinning of the splice. A rapid stretching of the splice to high extension is not a reliable indication of splice strength relative to forming ring requirements.
- Knife entry and exit portions are generally the weakest spots of an innertube. To overcome this problem, several innertube manufacturers add a small thin strip of unvulcanized innertube compound on the knife entry and exit portions of the innertube. When the innertube is cured, these strips flow and become cured, which reinforce the knife entry and exit portions of the innertube splice joints.
- Guidelines on trouble shooting of uncured splice defects have been summarized and are shown in Figure 14.

15. Horizontal cut splicers with fixed clamps

Machines of this type are capable of producing an excellent splice. They are best suited for long runs of single sizes as the clamp's openings are not adjustable and the clamps must be changed for each flat width of innertube to be spliced. They are relatively slow but it is possible for a single operator to operate two machines, particularly if the machines have been completely automated. These machines require close attention to innertube extrusion tolerances to obtain uniform splicing.

16. Machine details

The machine is made in three sizes covering innertube flat widths of 65 to 156 mm, 130 to 414 mm and 360 to 600 mm.

Innertube dimensions

Any splicing machine, which does not have adjustable jaws, requires very close control on innertube flat width and thickness. If the innertube is too wide for the clamps, pinching with fold breakdown may occur. If the innertube is too narrow, misalignment of the folds is likely, resulting in a weak splice which is likely to open during forming. Excessive thickness of the innertube results in crushing and breakdown of the folds. It may also result in "stepping" due to the squeezing out of the innertube ends after cutting. An innertube which is too thin may move in the clamps during cutting, producing a wavy edge, and during butting, producing poor consolidation. It is recommended not to vary innertube dimensions by more than $\pm 5\%$ from the clamp dimensions.

Lap splicing

The lap splicing technique is a very versatile method of joining. It can easily be set up as a secondary line to a main butt splicing operation to handle low volume markets of special innertubes. Four operations are involved in making a lap splice, namely, skiving, buffing, joining, and consolidation of the splice. After the innertube has been cut to length, a beveled featheredge is made on the overlapping end of the innertube using a suitable skiving machine. The surfaces to be joined may be freshened by very light buffing with a rotary wire brush or grinding stone. The splice is consolidated in a pneumatic press, first across the folds, then with the innertube in the normal position.

Guidelines for the storage of unvulcanized extruded innertubes

After splicing, green innertubes should be carefully stored on racks. Large size or heavy gauge innertubes should have plastic cylinders or foam rubber "pillow" supports placed inside the folded ends to prevent collapse and fold breakdown. Storage time should not be longer than 24 hours and the storage environment should be clean.

Guidelines for splice chilling

Chilling of the crown area of the butt splice butyl innertube helps to increase its green strength and minimize any splice opening during subsequent forming operations. The most common method of chilling is by keeping the splice section over a pipe through which cooled brine at 0°C to 5°C is circulating. Other methods include chilled air flow directed at the splice or a brief dip in a mixture of isopropanol or acetone with solid carbon dioxide ("dry ice"). The innertube should be adequately supported during chilling. If folded, the fold should be supported with foam pillows or similar devices. Splices should not be over chilled, the chilling time being usually equivalent to the duration of the cure cycle. Chilling may produce condensation on the splice. Thus, care should be

taken to ensure that no moisture drops remain on the innertube when it is placed in the press. The presence of moisture in the press may cause weak splices and dimpling. The chilling operation can be avoided if the splice quality is adequate. Several innertube producers, using ECUISM type splicers, which usually give good splice quality, omit this step to increase productivity.

Guidelines for forming

Forming is the operation in which the uncured innertube is inflated to about 95% of its final cured volume before placing

the innertube in the press. Forming rings should be designed to minimize any expansion of the base of the innertube, concentrating the expansion on the thickened crown section. Innertubes are to be slowly inflated over about a 30 second interval or, alternatively, inflated in two stages with about a 20 second pause in between stages. It is advisable to use a limit switch cut off to control the degree of inflation. Over formed innertubes are susceptible to thinning and may crease in the mold. If possible, the forming rings should not be located close to presses as the heat from the press may cause splice opening or thinning.

Figure 14

Universal innertube splicers: suggested correction of uncured splice faults

Fault	Cause	Remedy
Uneven or wavy cut	Knife too cold Tube slipping in jaws Knife angle incorrect Cutting speed too high Worn ball screw Bent screw Excessive tube end overhang before cut	Raise high heat current Increase clamp pressure Correct angle of knife Reduce cutting speed Replace/repair knife Reduce overhang
Tailed cut at exit fold	High-low heat transition too early Knife slowdown too late Slow speed too high	Retard high-low heat transition point Advance knife slowdown point Reduce knife slow speed
Deformed entry fold cut	Knife too cold at entry Knife slowdown too late. Slow speed too high. Knife too hot at entry scrap chute touching tube	Reduce high heat delay. Advance slowdown timer. Reduce knife slow speed. Increase high heat delay period
Opening at entry fold	Talc ejected from fold by high clamping pressure	Reposition scrap chute Minimize talc
Pinched splice	Jaws too tight Clamping pressure(s) too high	Adjust carefully Flatten folds Reduce clamp pressures
Fold break-down	Poor compound Excessive porosity	Improve compound More careful extrusion
Stepped splice	Tube thickness variation Misaligned jaws No slowdown on table closing	Improve extrusion control Shim jaws in line Adjust slowdown
Rind	Excessive overhang after cut. Excessive butting pressure. Fatigued rubber faces	Reduce knife clearance Lower butting pressure Change jaw faces

Guidelines for curing of innertubes

Innertubes are vulcanized in simple presses, often with a hot block to increase the temperature in the thicker valve region. Air pressure is applied internally to the innertube. The pressure can be up to 7 to 8 Bar. Low air pressure can result in the innertube wall flowing over the valve, whilst an excessively high air pressure can force the innertube into the mold parting line, produce excessive flash, and cause a localized deformation or gauge thinning around the innertube.

Innertubes are sometimes inflated internally with steam to gain a cure time reduction. Butyl rubber innertube curing temperatures of 175°C to 185°C are suggested and curing time will vary with size and thickness. Typical passenger innertubes are cured for 3.5 to 5 minutes and truck innertubes 6 to 8 minutes including blow down time.

Mold surfaces should be smooth and clean, both from the standpoint of the appearance of the finished innertube and from the ease with which the stock flows in the mold. Dirty molds can lead to poor stock flow and buckles. Sandpaper or steel wool should be avoided in cleaning the molds, as these cause scratches in the mold which may be quickly filled with foreign deposits.

A combination wax-abrasive material applied with a cloth buffing wheel is suggested. Molds should be well vented and the vents kept clear to prevent dimpling. An example of an innertube vulcanization press is shown in Figure 15.

Figure 15

Innertube vulcanization



Guidelines for inspection

After curing, the innertubes should be inspected carefully for flaws that may affect serviceability using a combination of visual and manual techniques. Particular attention should be given to the splice and to the valve region, which are the most common source of defective innertubes.

The innertubes are then usually vacuum evacuated, folded and packaged for storage and shipment. After the vacuum operation the innertubes should be inspected for any leakages.

Deflation of the innertube by vacuum is a good test to check innertube leaks. Leakage can be seen if air flows into the innertube during the vacuum operation. In the event of a leak, the innertube should be inflated and tested for any pinhole leaks and then sent for repair or scrap. Some manufacturers check all of the inflated innertubes in a water bath to check for leaks following the vacuum operation. The innertubes are then dried and packaged. High pressure vacuum evacuation of innertubes can cause high degrees of stress at the fold area of the innertube and this may result in cracking during storage in warehouses.

Guidelines for packaging

Following the quality assurance inspection, a good practice is to package the innertubes in sealed, preferably black or colored polyethylene bags, printed with the innertube size for identification. This will help maintain quality and prevent innertubes from potential degradation caused by ultra-violet light, moisture, oxygen, or ozone during long storage. After packaging, the innertubes are usually stacked in bulk in a cardboard box or polypropylene or polyethylene sack to prevent any damage during transit and prevent moisture, water, or other foreign material contamination.

6. Butyl rubber in bicycle innertubes

Bicycle innertubes cover a range of small section innertubes used on bicycles, motorized bicycles (mopeds) and small motorcycles. These innertubes are characterized by high inflation pressure, thin walls and high surface area to volume ratio. This can lead to rapid air loss when the innertubes are made of natural rubber and SBR rubber. Thus, the superior air retention properties of butyl rubber offer particular advantages for bicycle innertubes (Table III). Some guidelines on compounding are summarized below.

Polymers

The polymer is selected for a balance of processing characteristics, thinning resistance, cure rate, and required physical properties. An additional requirement for bicycle innertubes is green strength, necessary to ensure resistance of the thin walled innertube to damage or collapse during extrusion and subsequent processing. EXXON™ Butyl 268 can be suggested as a starting polymer in developing a formula. Examples of how this polymer can be used in bicycle tire innertubes are illustrated in the formulary in the website, www.butylrubber.com¹¹.

Carbon black

Carbon black is selected to give fast and smooth extrusions with adequate green strength to the compound. In the model formulary, N660 (70 phr) and N550 (50 phr) are suggested (Table XIII). The illustrated compounds show modulus properties at 100% extension below 1.0 MPa which is likely to give adequate splicing strength during processing and service.

Mineral fillers

Mineral fillers, such as whiting or soft clay are sometimes added to butyl rubber bicycle innertube compounds as an inert filler. However the benefit is often offset by an increase in scrap and reject levels. Where increased filler loadings are required, an increase in carbon black from 60 phr to 85 to 90 phr with an appropriate oil level adjustment can often be made.

Process oils

Paraffinic or naphthenic oils are preferred for butyl rubber innertube compounds. They are used at a lower level than in compounds for passenger and truck innertubes, to maintain a required green strength.

Cure systems

Conventional sulfur, TMTD, MBTS, and ZEDDC cure systems have been used for tire innertubes¹⁸. However, depending on compound requirements and factory processing conditions, a combination of sulfur, 1,3-dibutylthiourea (DBTU) and MBTS could be considered²⁰. This model cure system is shown in the

model formulary for bicycle innertube, and in the website formulary, www.butylrubber.com¹¹. Accelerator abbreviations are listed in Appendix 2.

Guidelines for processing and manufacturing of butyl rubber bicycle innertubes

Bicycle innertubes have thin walls. Therefore, particular attention is required to optimize carbon black dispersion and to eliminate foreign matter from the compound.

1. Masterbatch mixing

The basic principles for optimum mixing of bicycle innertube compounds are the same as those discussed in the previous chapters for the automobile innertubes.

2. Straining

Effective straining of bicycle innertube compounds is important. The screen pack should be at least 60 mesh (Table X). In some plants 120 mesh screens are used. Strainer throughput is lower than that of compounds for larger innertubes due to the fineness of screens, and the higher viscosity of the compound¹⁷. Slower extrusion rates or higher extrudate temperatures usually result from these two factors. Straining of finalized compounds should be avoided to prevent compound scorch.

3. Final batch mixing

The addition of the curatives on a thoroughly cleaned mill at a temperature below 125°C is suggested. Compound for hot feed extrusions is finalized and used directly from the mill. Compound for cold feed extrusions must be cooled as rapidly as possible with chilled water. All the water should be blown off prior to use in the cold feed extruder. Finally, a dry dusting agent should be applied to prevent sticking of the compound.

Guidelines for extrusion

Bicycle tube extrusions can be done on either cold feed or hot feed extrusion systems. Briefly:

- *Hot feed extrusion:* hot feed extrusion of bicycle innertubes requires the same care in feed strip preparation to minimize porosity as in the extrusion of passenger and truck innertubes. A feed strip of adequate size should be supplied and force feeding at the extruder feed box using a power roller is advantageous. It is suggested that the feed strip be at 80°C to 90°C, barrel and screw temperature 50°C to 60°C and die 100°C to 110°C. Multiple extrusions of smaller section bicycle innertubes are often used. Dual die heads are quite common. Talc or other anti-tack dusting agents are injected into the innertube during extrusion. The

innertubes should be cooled after extrusion. Dry, external dusting can be practiced but passing through 1% aqueous solution of a surfactant (liquid soap solution) has also been reported to be satisfactory.

- *Cold feed extrusion:* cold feed extruder (vented type) for bicycle innertubes are preferred for effective air expulsion. The screws of cold feed vented extruders consist of three principal zones. The first zone has a feed and plasticizing function. The second is a vacuum degassing zone to reduce volatile content, principally contained air. The third zone of the screw compresses the stock and feeds it to the head and die area. Suggested temperatures for butyl bicycle innertube extrusions are: (i) feed/plasticizing zone 50°C to 60°C, (ii) degassing 100°C to 120°C, (iii) compression zone 60°C to 70°C, (iv) the extruder head at around 110°C. The high temperature in the vacuum degassing zone serves to remove trapped air and improve the gas impermeability of the butyl compound.

Guidelines for valve installation

Press-cured innertubes use miniature versions of the valves with pre-cured rubber pads as used in automobile innertubes. Cements and application technology are similar to that for automobile innertubes as discussed earlier. An example of a bicycle innertube valve is shown in Figure 16.

Figure 16



Rubber covered innertube valves-bicycle

Guidelines for splicing

Press-cured bicycle innertubes are generally spliced before vulcanization. Metal clamp, vertical cut butt splicers are commonly used for splicing. Vertical cut, metal clamp splicers have short cycle times (8 to 10 seconds) and can produce good quality splices. The clamps are usually adjustable. In some designs, the flat width adjustment is limited and two or three sets of quickly changed adjustable jaws are provided. Models exist which will splice six innertubes simultaneously. Considerable operator expertise in loading such machines is frequently required to obtain their full output.

Guidelines for vulcanization

Depending on the compound cure system, press-cured innertubes can be vulcanized at 170°C to 185°C with cure times in the range of 3 to 4 minutes. Innertubes for autoclave cure are usually mounted on mandrels with the aid of compressed air. Cure times are normally longer than those for press-cured innertubes due to a slower warm-up. Pressure limitations on the autoclave may also extend cure times. It is possible to manufacture bicycle innertubes using continuous vulcanization (CV) techniques such as salt baths or by microwave. The cured innertube is then lap spliced using an adhesive. However, due to the lower productivity associated with lap splicing, continuous vulcanization systems are not commonly used for innertube manufacture.

Guidelines for inspection and packaging

As noted earlier, after quality assurance inspection, the innertubes can be packaged in a sealed, preferably black or colored polyethylene bag, with innertube size labels for identification. This will help maintain quality and protect the innertubes from potential degradation due to ultra-violet light, moisture, oxygen, or ozone during long storage. After packaging, the innertubes are usually stacked, in bulk, in a cardboard box or polypropylene or polyethylene container to prevent any damage during transit and avoid moisture, water, and other foreign material contamination.

Table XIII

Model compounds or bicycle tire innertubes using EXXON™ butyl 268 carbon black grades N550 and N660

Material	Test Method Based On	Units and Cond. (2)	1	2
			N550	N660
Material		Units	Amount	Amount
EXXON Butyl Grade 268		PHR	100.00	100.00
Carbon Black N550		PHR	50.00	
Carbon Black N660				70.00
Parafinic oil		PHR	20.00	25.00
Alliphatic Tackifying Resin		PHR	3.00	3.00
Stearic acid		PHR	1.00	1.00
Zinc Oxide		PHR	5.00	5.00
Mercaptobenzothiazyl disulfide (MBTS)		PHR	1.00	1.50
1,3-Dibutylthiourea (DBTU)		PHR	2.00	3.00
Sulfur		PHR	2.00	2.00
Total (PHR) (1)			184.00	210.50

Properties	Test Method Based On	Units and Cond.	Typical Values	Typical Values
MooneyViscosityML1+4	ASTM D1646	MU at 100°C	46.2	42.6
Mooney Scorch	ASTM D1646	at 125°C		
Minimum viscosity		MU	34.1	33
Time to 5pt rise		Minutes	14.2	14.7
Time to 10pt rise		Minutes	18.4	19.6
Rheometer (ODR)	ASTM D2084 160°C, 60 minutes, 3.0°arc			
MI (Minimum torque)		dNm	8.7	7.8
Mh (Maximum torque)		dNm	50	47.8
Mh-MI (delt torque)		dNm	41.3	40
ts2 (time to 2 point increase)		Minutes	2.2	2.3
Tc50 (time to 50% torque increase)		Minutes	15.3	15.2
Tc90 (time to 90% torque increase)		Minutes	43.9	41.8
Rheometer (ODR)	ASTM D2084 180°C, 30 minutes, 3.0°arc			
MI (Minimum torque)		dNm	8.1	7.2
Mh (Maximum torque)		dNm	48	47.8
Mh-MI (delt torque)		dNm	39.9	40.7
ts2 (time to 2 point increase)		Minutes	1.1	1.1
Tc50 (time to 50% torque increase)		Minutes	4.4	4.6
Tc90 (time to 90% torque increase)		Minutes	13	13.3

Rheometer (MDR)	ASTM D5289 160°C, 60 minutes, 0.5°arc			
MI (Minimum torque)		dNm	1.4	1.4
Mh (Maximum torque)		dNm	9.1	10.3
Mh-MI (delt torque)		dNm	7.7	8.9
Tc50 (time to 50% torque increase)		Minutes	12.8	14
Tc90 (time to 90% torque increase)		Minutes	42	44.6
Rheometer (MDR)	ASTM D5289 180°C, 30 minutes, 0.5°arc			
MI (Minimum torque)		dNm	1.2	1.3
Mh (Maximum torque)		dNm	8.6	10.5
Mh-MI (delt torque)		dNm	7.4	9.2
Tc50 (time to 50% torque increase)		Minutes	3	3.5
Tc90 (time to 90% torque increase)		Minutes	10.2	9.4
Cured 25 minutes at 160°C (2)				
Tensile Strength	ASTM D412	MPa	13.1	10.9
Elongation at Break		%	800	765
Modulus 100%		MPa	0.8	0.9
Modulus 200%		MPa	1.5	1.7
Modulus 300%		MPa	2.4	2.7
Energy at Break		Joules	10.9	9.4
Tear Strength (Die B) Mean	ASTM D624	KN/m	34.1	39.2
Tear Strenght (Die C) Mean		KN/m	30.3	30.7
Hardness	ASTM D2240	Shore A	41	45
Aged 125°C x 72 hrs				
Tensile Strength	ASTM D412	MPa	9.7	7.4
Elongation at Break		%	665	545
Modulus 100%		MPa	1.4	1.7
Modulus 200%		MPa	2.8	3.3
Modulus 300%		MPa	4.2	4.5
Energy at Break		Joules	8.6	6.4
Aged 125°C x 72 hrs				
Tear Strength (Die B) Mean	ASTM D624	KN/m	30.1	21
Tear Strenght (Die C) Mean	ASTM D624	KN/m	26.1	27.4
Aged 125°C x 72 hrs				
Hardness	ASTM D2240	Shore A	50	58
Air permeability at 65°C	ExxonMobil Method	cc[CSTP] mm (m³ x 780 mm Hg Hour)	12.2	13.5
Green strenght	ExxonMobil Method	gms/1.5mm Time to 50% decay in seconds	528 38.3	481 27.4

Source: www.butylrubber.com.

7. Heat resistant chlorobutyl rubber innertube

Innertubes made from butyl rubber and vulcanized with sulfur have good heat stability and physical properties. However, high ambient temperatures in tropical countries and severe service conditions, such as found with long haul and heavily loaded trucks, can cause repeated expansion and contraction of innertubes fitted in tires. As a result, innertubes made from sulfur cross-linked butyl rubber or butyl rubber-EPDM blended compounds may degrade, lose air, and can adversely affect the overall tire performance. Chlorobutyl rubber crosslinked with zinc oxide offers improved resistance to heat softening and growth while maintaining the required butyl rubber properties of air retention and long service life for innertubes^{21,22}.

Guidelines for compounding and processing

Processing of chlorobutyl is the same as that for butyl rubber innertube compounds. However, some minor changes are suggested and discussed below. The modifications pertain to mixing, valving, and curing. Chlorobutyl innertubes can be cured with zinc oxide, unlike butyl rubber, which is crosslinked with sulfur¹⁵. As a guideline, a suggested model formula for a high heat resistant truck innertube together with typical processing and physical properties is shown in Table XIV¹¹.

Cure system

The zinc oxide cure system in chlorobutyl is a very simple cure system and the following points are noted:

- The zinc oxide cure is sensitive to acidic and basic compounding ingredients. In general, acids will accelerate cure, whereas, bases will retard.
- Zinc oxide forms -C-C-bond crosslinks, which have better heat resistance compared to sulfur crosslinked elastomers.
- Addition of magnesium oxide improves scorch safety¹⁵.
- A suggested model chlorobutyl innertube compound cure system can consist of zinc oxide (5.0 phr) and zinc dibenzylthiocarbamate (ZBEC) at 2.0 phr (Table XV). Additional starting point development formulations can be found at 'www.butylrubber.com'¹¹.

Guidelines for mixing

Like butyl rubber innertube compound mixing, chlorobutyl rubber innertube is also mixed in two stages (as shown below):

Stage 1: Master batch mixing:

Sequence: 0 min. - polymer + MgO

0.5 min. - 2/3 black

2.5 min. - 1/3 black + Oil + Stearic Acid

3.5 min. - dump 140 to 145°C

It is recommended to dump chlorobutyl compound

masterbatches between 140°C and 145°C. Dump or drop temperatures higher than 150°C may result in dehydrohalogenation that may have a detrimental effect on final compound properties.

Stage 2: Final batch mixing:

Sequence: 0 min. - master batch and zinc oxide
+ ZBEC accelerator.

2 min. - dump at below 105°C.

Guidelines for straining, extrusion, valving, splicing

Guidelines on straining, extrusion, valving, and splicing of chlorobutyl rubber compounds and tire innertubes are the same as that for butyl compounds.

Guidelines for vulcanizing

Vulcanizing operations such as forming and molding of chlorobutyl innertubes are almost the same as butyl rubber innertube curing as described earlier, with the following suggested guidelines.

- It is suggested that hot air be used as an internal heating medium for chlorobutyl rubber innertubes rather than steam. In general, to improve output of chlorobutyl rubber innertube production, the curing press is heated (with steam) close to 200°C and hot air is used as internal heating medium to avoid the formation of hydrochloric acid, which may degrade the inner surface of the innertube during service. Chlorobutyl rubber has good mold flow and mold release properties.
- In the event of a mold sticking problem, the level of stearic acid may be increased from 1.0 phr to 1.5 phr. Chlorobutyl rubber innertubes may vulcanize more rapidly than regular butyl rubber. A cure time reduction of 1 to 2 minutes has been reported depending on the tube thickness and curing temperature. Zinc oxide curing of chlorobutyl rubber innertubes may lead to mold staining due to the formation of zinc chloride.
- It is known that hard chrome plating of curing molds helps to minimize staining problems. It is suggested that the mold is cleaned at regular intervals, as specified by the mold manufacturers and producers of mold release agents. Stained curing molds may introduce visual imperfections that may cause innertubes to be scrapped at the end of the manufacturing process.

Advantages of chlorobutyl innertubes during service

Chlorobutyl rubber innertubes, when compared to regular butyl innertubes, show better resistance to heat softening. Chlorobutyl rubber innertubes can perform better in higher tire mileage applications and show better retention of physical properties. Therefore, some advantages of chlorobutyl over regular butyl could be listed as follows:

- Butyl rubber truck innertubes at temperature above 140°C tend to soften and stick to tire during service, which chlorobutyl rubber innertubes do not.
- Chlorobutyl rubber tension set properties are lower suggesting lower growth during service which is beneficial for truck tire innertubes used in tires of long haul vehicles and heavily loaded trucks.
- An inherent characteristic of chlorobutyl polymer is the ability to withstand prolonged service at elevated temperature with relatively little degradation of properties.

Table XIV

Suggested model formulation for a truck innertube
 EXXON™ chlorobutyl grade 1066, ZBEC vulcanization system

Material	Units	Amount
EXXON Chlorobutyl Grade 1066	PHR	100.00
Carbon Black N660	PHR	75.00
Napthenic Oil	PHR	28.00
Magnesium Oxide	PHR	0.50
Zinc Oxide	PHR	5.00
Zinc dibenzylthiocarbamate (ZBEC)	PHR	2.00
Total (PHR)		211.50

Properties	Test Method Based on	Units and Conditions	Typical Values
Mooney Viscosity ML 1+4	ASTM D1646	MU at 100°C	38.3
Mooney Scorch	ASTM D1646		
Minimum viscosity		MU at 125° C	28.8
Time to 5pt rise		Minutes	29.7
Time to 10pt rise		Minutes	33.9
Rheometer (ODR)	ASTM D 2084 160°C, 60 minutes, 3.0° arc		
MI (Minimum torque)		dNm	6.8
Mh (Maximum torque)		dNm	26.7
Mh-MI (delta torque)		dNm	19.9
ts2		Minutes	2.1
Tc25 (time to 25% torque increase)		Minutes	3.2
Tc90 (time to 90% torque increase)		Minutes	14.6
Rheometer (MDR)	ASTM D5289 160°C, 60 minutes, 0.5° arc		
MI (Minimum torque)		dNm	1.3
Mh (Maximum torque)		dNm	5.4
Mh-MI (delta torque)		dNm	4.1
Tc25 (time to 25% torque increase)		Minutes	1.6
Tc90 (time to 90% torque increase)		Minutes	9.2
Rheometer (MDR)	ASTM D5289 180°C, 60 minutes, 0.5° arc		
MI (Minimum torque)		dNm	1.1
Mh (Maximum torque)		dNm	4.4
Mh-MI (delta torque)		dNm	3.3
Tc25 (time to 25% torque increase)		Minutes	0.6
Tc90 (time to 90% torque increase)		Minutes	2.3

Properties	Test Method Based on	Units and Conditions	Typical Values
Cured 17 minutes at 160°C			
Tensile Strength	ASTL D412	MPa	7.7
Elongation at Break		%	530
Modulus 100%		MPa	0.9
Modulus 300%		MPa	4.3
Energy at Break		Joules	5.4
Tear Strength - Die C	ASTM D624	KN/m	26.3
Hardness	ASTM D2240	Shore A	42
Aged 125° C x 72 hrs			
Tensile Strength	ASTM D412	MPa	7.5
Elongation at Break		%	450
Modulus 100%		MPa	1.3
Modulus 300%		MPa	5.3
Energy at Break		Joules	4.8
Aged 125° C x 72 hrs			
Tear Strength - Die C	ASTM D624	KN/m	23.1
Aged 125° C x 72 hrs			
Hardness	ASTM D2240	Shore A	46
Aged 150° C x 24 hrs			
Tensile Strength	ASTM D412	MPa	7.2
Elongation at Break		%	435
Modulus 100%		MPa	1.4
Modulus 300%		MPa	5.3
Energy at Break		Joules	4.3
Aged 150° C x 24 hrs			
Tear Strength - Die C	ASTM D624	KN/m	23.2
Aged 150° C x 24 hrs			
Hardness	ASTM D2240	Shore A	50
Tension Set (ExxonMobil Method)	Method-A	%	6
Tension Set (ExxonMobil Method)	Method-B	%	8.1
Air permeability at 65° C	ExxonMobil Method	cc[STP].mm/ (m ² x 760 mm Hg Hour)	25.7
Green strength	EM Method	gms.1.5mm	397
(ExxonMobil, EM, Method)	Time to 50% decay in seconds		15.6

Values: values given are typical and should not be interpreted as a specification.

PHR: parts per hundred rubbers.

Source: www.butylrubber.com¹¹

8. Guidelines for trouble shooting innertube processing and manufacturing

Factory compound processing difficulties tend to center around compound viscosity, milling operations, and innertube gauge control. Potential challenges the factory engineer may encounter with possible solutions are listed below. Figure 17 also provides a template upon which more specific trouble shooting guidelines can be developed to meet the requirements of a particular factory operation.

Variations in compound viscosity

Mooney viscosity variation of compounds can cause problems in extrusion, splicing, and forming of innertubes. For example, large variations in compound viscosity can occur as a result of cure system variation. This variability can occur when the same internal mixer is used to prepare both the compound masterbatch and final productive mix containing the curatives. Powdered curatives may collect at the intake of the dust removal system of the internal mixer and later fall back into the mixer during subsequent mixing operations. If this occurs during mixing of the innertube masterbatch, the combination of curatives and high mixing temperatures can result in a condition of partial cure, pre-cure, or scorching. Even at low curative levels, the effect will be to increase the Mooney viscosity of the compound. The immediate solution to the problem is to prevent contamination of the masterbatch by the curatives.

Variable viscosity can also result from poor filler dispersion, or from variations in the level of work-away, rework (scrap), or stock being returned to the processing operations. In addition to causing variations in the viscosity of the unvulcanized compound, accelerator contamination of the innertube masterbatch can also result in differences in the cured modulus. To illustrate this, in a controlled experiment, 0.2 parts of accelerator added to the masterbatch in a 175°C mixing operation caused an increase of 9 points in Mooney viscosity and an increase of 1.5 MPa in 300% modulus value. The same number of additional curatives added in a normal low temperature (i.e. less than 150°C) mixing operation showed no effect on either the viscosity of the stock or the cured modulus¹⁸.

Strainer screen plugging

Normal practice in innertube production plants is to change the strainer screen approximately once per shift. At times, however it has been found necessary to make changes as frequently as every hour due to plugging of the strainer screen. A common cause of such rapid plugging has been found to be poor dispersion of some ingredient, usually the carbon black. Suggested steps that could be taken in overcoming these problems are:

- Check the quality of the carbon black to ensure that the pellet hardness or other properties like grit content of the black have the proper specified values,
- Increase the length of the mixing cycle
- Delay oil addition until the carbon black has been dispersed in the rubber, or,
- Change the black type to one that is more readily dispersed⁹.

Mill bagging

The bagging of butyl rubber innertube stocks on the mill is frequently associated with the use of a compound having excessively high carbon black and oil. Should this condition be a problem, the suggested solution is to increase the viscosity or the nerve of the compound. This is most easily done by adjusting the amount of carbon black, reducing the quantity of oil, or both.

An alternative approach may be to reduce the temperature of the compound on the mill. This might be accomplished through the use of more cooling water, or the use of cooling water at a lower temperature. If feasible, a change in the mill roll ratio or speed may also be helpful. Another approach would be the use of rework added to the internal mixer. This should be carefully controlled in order to avoid variations in viscosity that can cause other concerns.

Die plating

A build-up of material on the extruder die can cause a gradual change in the dimensions of the extruder innertube, eventually requiring that the extrusion line be shut down while the die is either cleaned or adjusted in order to return to the proper innertube dimensions and weight. Analysis of such die build-up material usually shows it to be high in inorganic materials. Spectrographic analysis of these materials frequently shows a high percentage of clay, which apparently tends to accumulate on the extruder die.

Under typical conditions, clay is not a component of the innertube compound nor is it used during the processing of innertubes. However, occasionally the talc, which is used to dust the extruded innertubes, may contain minor amounts of clay. The practice of including reworked material with fresh stock during extrusion of innertubes provides a route for such clay to reach the extruder. To help prevent this problem, clay-free talc could be used. Die plating will also occur if calcium carbonate fillers are used in the compound.

Variable innertube width

Variations in extruded innertube width have frequently been due to excessive stretching of the innertube during the

extrusion operation. This can occur when the innertube is passed over a succession of conveyor belts not operating at synchronized speed. It is necessary to minimize the amount of stretch needed to properly control the innertube dimensions. Mooney variance and extruder starvation may also lead to excess stretch-down even when the take-off conveyors are operating satisfactorily.

Dimension or gauge variation has been observed when some aromatic process oils have been used in butyl innertube compounds. Therefore, aromatic process oils are not used to any great extent in butyl rubber innertube compounds. Paraffinic and naphthenic oils tend to be preferred. Adequate attention to masterbatch mix quality can help minimize problems. Another possible cause of variation is addition of rework which has variable viscosity.

Uncured innertube blisters

The most common cause of blisters in the uncured extruded innertube is trapped air. This trapped air is frequently the result of an excessively soft compound. This compound softness can be due to either the formulation being employed or to the processing temperatures, particularly on the mills feeding the extruder. It is suggested that the stock temperature leaving the final mill prior to the extruder be approximately 90°C. Temperatures substantially above this level have been found to contribute to an excessive amount of air being trapped by the stock on the mill and carried into the extruder from which it emerges as blisters in the innertube.

In order to control the stock temperature on the mills within the desired range, in some cases it may be necessary to consider equipment setup adjustments. That is, either the friction ratio between the front and rear rolls of the mills may need to be changed or the overall roll speeds may need adjustment. Alternatively, consideration can be given to compound formulation changes enabling an increase in the green strength of the compound.

Another known cause of blisters in uncured innertubes is moisture in the stock being fed to the extruder. This moisture is most often traceable to wet slabs of compound being used to load the warm-up mill on the extruder line. It is suggested that care is taken to use only dry stock in feeding the extruder.

Cold flow and bruising

Unvulcanized butyl rubber is subject to flow under load. Therefore, in all operations subsequent to extrusion, unvulcanized innertubes should be handled with care. Excessive stacking or prolonged storage should be avoided in order to minimize the effects of cold flow and bruising which can lead to thin spots in the cured innertube or even failure of

the green innertube during forming. Green strength promoters such as poly-*para*-dinitroso benzene (DNB) on an inert carrier can be used to increase the green strength of the innertube stock to improve its resistance to cold flow and bruising. It is added to the compound early in the mix. DNB partially crosslinks the polymer, giving an effect similar to increasing the molecular weight of the polymer. This increases the tolerance of the compound for high carbon black and oil loading without excessive cold flow or bruising of the uncured innertube stock.

Fold breakdown

Fold breakdown, a condition caused by creasing of the innertube under its own weight, is related to cold flow and bruising. An effective means of controlling this condition is to limit the storage times after innertube extrusion and splicing. This limit in storage time should be balanced against improvements in splice strength, which may be realized by a longer storage period between splicing and curing. If modifications in the factory operations are not sufficient to overcome the fold breakdown or related problems, then compound modifications may be required. Potentially helpful modifications include reductions in the loading of carbon black and oil, or a partial or full replacement of the carbon black type to a lower structure filler.

Splice defects

A frequent cause of defective splices is misalignment of the clamps and dies holding the innertube during the splicing operation. This type of splice defect is usually visible in the uncured innertube as a step or offset area at the splice. The solution to this problem is to maintain the splicing machine in proper settings. The settings should be checked periodically during innertube production and adjustments made as needed.

Buckle and mold pinching

Buckles in a cured innertube are generally caused by the uncured innertube being too large for the mold. The oversized green innertube can be due to oversized innertube extrusion or due to forming under high pressure causing the rubber to stretch more than the normal. In addition, the use of a compound that is excessively soft can result in innertubes being stretched too much even under normal pressures. The presence of these conditions will indicate a need to check the uncured innertube dimensions, and if necessary, adjust the formulation in order to avoid excessive softness. The use of limit switches during forming operations may also help to overcome this problem.

In addition to buckles, an oversized green innertube can result in the innertube being pinched between the two halves of the mold as it closes. This pinching causes a loss in gauge of the

innertube along the mold parting line. In the most severe case, the thinning can be such that the innertube will fail under very low internal pressure. In some cases, buckles and pinches in cured innertubes can also be the result of excessive stiffness which prevents the extruded innertube from forming into the proper shape for curing. If this problem is encountered, Mooney viscosity of the compound should be checked to ensure that the compound has not scorched. In some cases, it may be necessary to reformulate to overcome the problem.

Dimpling

Dimpling, or the presence of cavities in the surface of cured innertubes, is thought to be due to localized areas of trapped vapor or air between the innertube and the mold. To avoid this problem, the mold should be sufficiently well vented to allow gases to escape and the vents kept open. Periodic inspection of molds for plugged vents is suggested. In addition, the dusting agents used on the surface of the innertube can have an influence on the problem. Large particle size, coarse dusting agents aid the escape of gases from between the innertube and the mold.

Ghosting

"Ghosting" is a condition in which a label printed on an uncured innertube transfers from the innertube to the mold during curing and then back to other innertubes cured subsequently. In order to avoid this problem, a common practice is to label innertubes after vulcanization.

Splice rind cracking

Rind formation is a characteristic of steel clamp splicers and has been discussed earlier. The most common cause of cracked rind is excessive overhang at the time the ends of the innertube are trimmed prior to splicing. The most direct means of avoiding this situation is either to reduce the amount of overhang or to trim the rind with a hot knife after the innertube has been spliced. There is evidence that trimming the rind will also result in improved splice durability, perhaps because any weak spot resulting from a cracked rind is eliminated. An additional procedure, which can be used, is to paint the rind area with cement prior to curing. However, there is some hazard involved in doing this since the solvent used in the cement can weaken the uncured splice and may cause it to partially or completely open during the forming step.

Another common cause of rind cracking is contamination, which may prevent the surface of the rubber from curing. The use of zinc stearate for exterior dusting usually eliminates rind cracking. Condensation on the innertube during and immediately following the chilling of the splice area is another source of contamination and potential source of final product defect.

Under valve porosity

There are two varieties of porosity beneath the valve. The first manifests itself predominantly at the valve pad/innertube wall interface and is associated with trapped air, freshener, cement volatiles, or less frequently with uncured cement solids. The second type of porosity extends throughout the innertube wall and is caused by under-cure of the innertube itself.

Air entrapment is sometimes caused by the use of a high viscosity valve cement, particularly when it is applied to the valve base by brushing. This problem can be avoided by applying the cement as a spray. If it is necessary to apply the cement by brushing, care should be taken to avoid excessive application of cement. Adjusting the viscosity of the cement may be helpful in this respect. Brushes can be cleaned at each shift change and replaced as needed. Increasing the applied pressure dwell time during valve attachment to the innertube may help reduce air entrapment and subsequent porosity under the valve.

Solvent is frequently used to freshen the innertube valve area prior to attachment of the valve. If the solvent is not given sufficient time to evaporate before applying the valve, porosity can develop at the interface during the cure. Solvent can also be present as a result of insufficient drying of cemented valves. Both problems can be overcome by increasing the drying time for the solvent or cement. An alternative to the solvent freshening is to place a small square of plastic over the valve area after the innertube has been extruded. When the plastic is removed, a clean, fresh surface is available for attaching the valve. Porosity due to low state of cure has several solutions. The simplest way is to increase the cure time or increase the hot block temperature if it is possible.

Ozone resistance

The amount of carbon black and oil in butyl innertubes has increased over the years leading to a decrease in the cross-link density of innertubes cured under constant temperature and time conditions. This decrease in cross-link density can have a detrimental effect on properties such as ozone resistance and this can lead to defective innertubes during storage in high ozone environments. When production limitations prohibit increasing the cross-link density by the use of a longer cure cycle or a higher cure temperature, an increase of 15 phr of EPDM, such as Vistalon™ 2504, may substantially improve the ozone resistance of innertubes. However, aged modulus may increase and splice life may be reduced. Hence this approach is not suggested for low modulus innertubes without adjustments to the compound composition.

A possible source of variation in the ozone resistance of innertubes is a mold that is operating at a lower temperature

than other molds in the same line, thereby causing a lower state of cure. The lower press mold temperature sometimes occurs when the mold is located at the end of the curing line and where it receives only a portion of the steam required to maintain full curing temperature. A reduced flow of steam may also be related to the mold being blocked or filled with water. Another source of lower mold temperature can be the practice of leaving the mold open for an extended period of time. This can permit parts of the mold to cool off with the result that the first innertube cured after this period may have a lower state of cure.

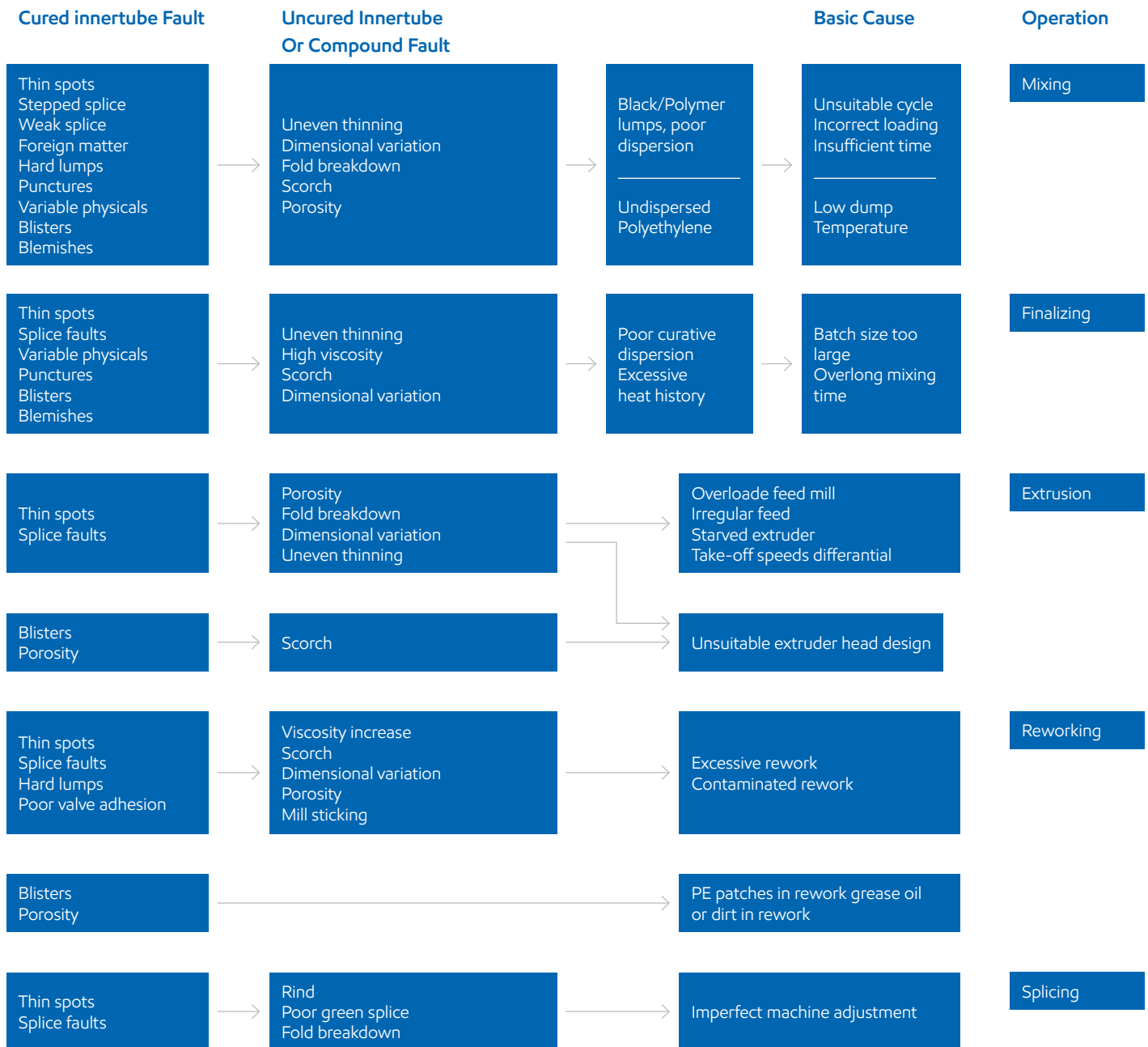
An additional cause of poor ozone resistance in butyl innertubes can be the use of butyl rubber innertube reclaim. This is thought to be due to some reclaiming oils used in the production of reclaim which may vary in unsaturation. The scrap innertubes from which butyl rubber reclaim is made can also contain repair patches made of highly unsaturated general-purpose rubber. If these patches are not removed from the innertube prior to the reclaiming process, they can contaminate the butyl rubber reclaim. This in turn affects the ozone resistance of the butyl rubber innertubes in which the reclaim is used.

Cured innertube faults

Quality control inspection of finished innertubes and laboratory testing can reveal a wide range of faults, such as thin spots, stepped splices, weak splices, foreign matter, hard lumps, punctures, variable physical properties, blisters, blemishes, poor valve adhesion, under valve porosity, creases or folds, valve overflow, high set, poor ozone resistance, poor heat resistance, poor appearance, weak spots, mold sticking and dimpling. An analysis of these faults, relating them to uncured innertubes and compound faults and indicating the basic cause, is given earlier. It should therefore be noted that many of the cured innertube faults and defects can arise from more than one cause.

Figure 17

Guidelines for correcting between cured innertube defects in processing and manufacturing operation





9. Flaps

Use of flaps is a good practice in assuring proper innertube performance. The flap is a rubber protector used with tube-type tires to prevent damage to the innertube resulting from direct contact with tire bead toes, the metallic rim, and the valve slot of the rim. The flap performance requirements include parameters such as:

- Good durability and flexibility.
- Aged hardening resistance: Hardened flaps may chip and the hard rubber with hard edges may cause cuts to the tube.
- Good compression set resistance, i.e. the flap must retain its profile against the wheel or rim in presence of high pressure and heat so as to ensure proper protection of the innertube.
- Good heat degradation resistance.

Frequently, new innertubes are supplied with replacement flaps. Depending on the size, the flap is mounted on a rim either by manually stretching the flap or mechanically placing the flap over the rim.

Flaps are produced by one of two methods. Molded flaps are used for small to medium truck tube-type tires. Extruded flaps cured in an autoclave are used on larger off-the-road (OTR) vehicle tire and wheel assemblies. As an example, such flaps would be used with tire sizes, 16.00R25 and larger. The molded or extruded flap will typically have a heavy centerline gauge, tapering out to the edge. Fabric reinforcement or heavy rubber gauge can be applied at the location of the valve stem outlet to minimize any abrasion due to the metal valve.

Flaps can be made from three types of compounds. General purpose rubber can be used when less severe service conditions are encountered. However, such flaps will tend to show age hardening and depending in the selection of polymers, a marching modulus. This could impact the long-term performance of the tube. Higher quality flaps are made from either butyl rubber or EPDM rubber. These flaps show better heat and aging resistance though butyl rubber compounds may tend to soften with time. The optimum performing flap would be a blend of butyl and EPDM rubber for maintenance of the range of required properties such as hardness, heat aging, and retention of compound mechanical properties.

10. Summary

The excellent performance of the modern tire innertube is possible due to the use of butyl rubber. Use of this polymer in the innertube compound has enabled improvements in air retention and improvements in tire durability. Butyl rubber and chlorobutyl rubber, also used in innertubes, represent special purpose elastomers requiring special handling procedures and precautions when processing the materials through tire innertube manufacturing plants. Such precautions include special mixing procedures, careful extrusion conditions, and policies to ensure no contamination. Poor formulating and processing conditions can lead to deterioration in innertube performance.

This manual is intended to provide information for formulating, mixing, and processing of butyl and chlorobutyl rubber compounds to produce a tire innertube. It also provides a basis for development of a check list of simple principles which when followed, may minimize scrap, help the factory engineer obtain required compound property targets, and assist in meeting the quality assurance specifications to which the innertubes are manufactured.

APPENDIX 1

Recognized industry abbreviations for elastomers^{9,14}

AU	Polyester urethane
BR	Polybutadiene
BIIR	Brominated isobutylene-isoprene rubber (bromobutyl rubber)
BHT	Antioxidant. Protects against degradation.
CIIR	Chlorinated isobutylene-isoprene rubber (chlorobutyl rubber)
CPE	Chlorinated polyethylene
CR	Chloroprene rubber
CSM	Chlorosulfonyl polyethylene
EAM	Ethylene-vinyl acetate copolymer
EPDM	Terpolymer of ethylene, propylene and a diene with a residual unsaturated portion in the chain
EPM	Ethylene propylene copolymer
EU	Polyether urethane
ESBO	Epoxidized soybean oil. Epoxy groups capture any acids, including excess stearic acid. Level is approx 1.3%
HNBR	Hydrogenated acrylonitrile butadiene rubber
IIR	Isobutylene isoprene rubber
IR	Synthetic polyisoprene
NBR	Acrylonitrile butadiene rubber
SBR	Styrene butadiene rubber
E-SBR	Emulsion styrene butadiene rubber
S-SBR	Solution styrene butadiene rubber
X-NBR	Carboxylated acrylonitrile butadiene rubber
X-SBR	Carboxylated styrene butadiene rubber
Y-SBR	Block copolymer of styrene and butadiene

APPENDIX 2Recognized industry abbreviations for accelerators^{9,14}

Abbreviation & commercial descriptions	Chemical name	Function
CB	N-cyclohexyl-2-benzothiazolesulfenamide	Primary Acc.
BCI-MX	1,3-bis(citraconimidomethyl) benzene	Reversion Res.
CTP	N-(cyclohexylthio) phthalimide	Retarder
DBQDO	p-quinone dioxime dibenzoate	Quinone Cure
DCBS	Dicyclohexylbenzothiazole sulfenamide	Primary Acc.
DETU	Diethylthiourea	
DBTU	Dibutylthiourea	
DOTG	Di-o-tolylguanidine	Secondary Acc.
DPG	Diphenyl guanidine	Secondary Acc.
DPPD	Diphenyl-p-phenylenediamine	Accelerator
DPTU	N, N'-diphenylthiourea	
DTDM	4,4-Dithiodimorpholine	Vulcanizing Agent
ETU	Ethylthiourea	Accelerator
HTS	Hexamethylene-1,6-bis(thiosulfate)	Reversion Res.
	Disodium salt, dihydrate	
MBS	Oxydiethylene benzothiazole-2	Primary Acc.
	-sulfenamide primary Acc.	
MBT	Mercaptobenzothiazole	Accelerator
MBTS	Mercaptobenzothiazole disulfide	Primary Acc.
QDO	p-quinone dioxime	Quinone Cure
TBBS	tert-Butyl-2-benzothiazole sulfenamide	Primary Acc.
TBSI	N-t-butyl-2-benzothiazole sulfenimide	Primary Acc.
TBzTD	Tetrabenzylthiuram disulfide	Secondary Acc.
TMTD	Tetramethylthiuram disulfide	Secondary Acc.
TMTM	Tetramethylthiuram monosulfide	Secondary Acc.
Amylphenol disulfide 1 Amyl disulfide polymer (23% S)		Sulfur Donor
Amylphenol disulfide 2 Amyl disulfide polymer (28% S)		Sulfur Donor
Amylphenol disulfide 3 Amyl disulfide polymer (18% S)		Sulfur Donor
Amylphenol disulfide 4 Amyl disulfide polymer (30% S)		Sulfur Donor
Amylphenol disulfide 5 Amyl disulfide polymer (27% S, 10% HSt)		Sulfur Donor
ZDMC	Zinc dimethyldithiocarbamate	Secondary Acc.
ZDEC	Zinc diethyldithiocarbamate	Secondary Acc.
ZDBC	Zinc dibutyldithiocarbamate	Secondary Acc.
ZBEC	Zinc dibenzylthiocarbamate	Secondary Acc.
ZIX	Zinc isopropyl xanthate	Low temp. Acc.
ZBPD	Zinc dibutylphosphorodithiate	Accelerator

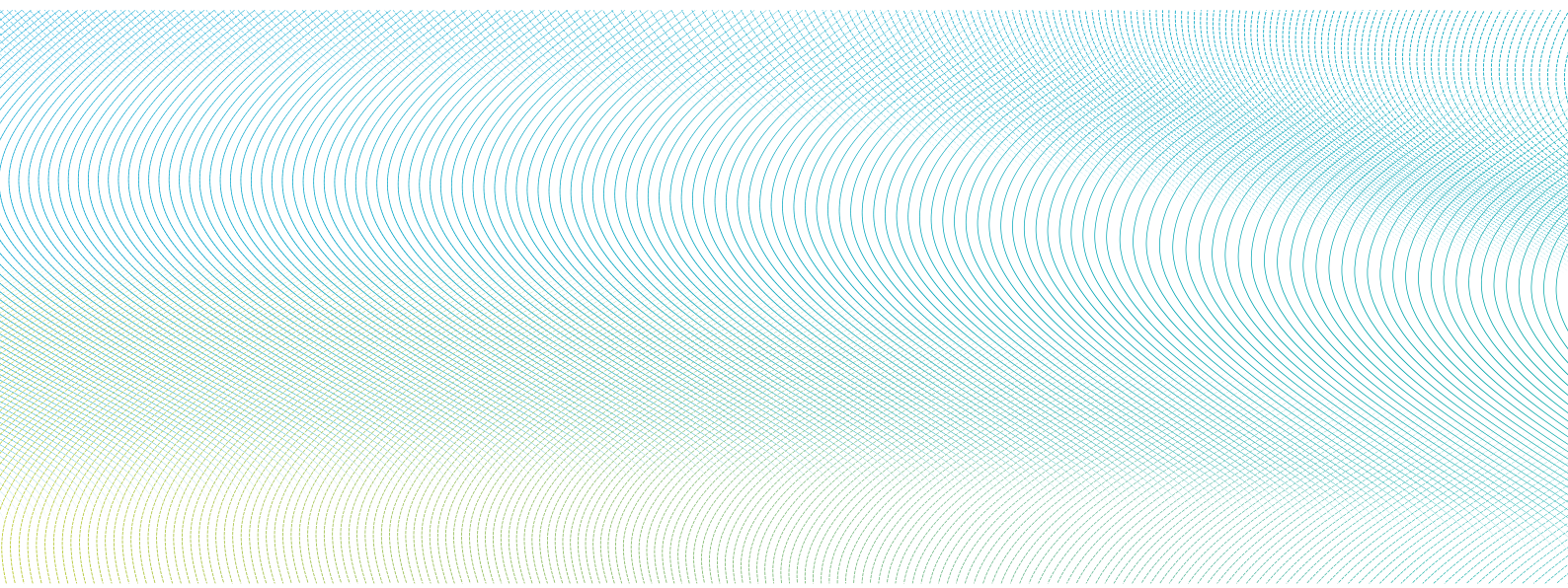
APPENDIX 3

ECUISM splicing machine licensed manufacturers

McNeil-Akron In	96 East Crosier St Akron, Ohio,44311, USA
Midland Design and Manufacturing	Health Mill Road Wombourne, Wolver Hampton, WV5 8AH, UK
Nakata Zoki Co.Ltd	1-20, 3-Chome, Wakinohama-cho chou-ku, Kobe, Japan
VMI-Epe-Holland B.V.	P.O. Box No-977, Mount Poonamalle Road, Meenambakkam, Chennai-600 089, India

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