Kirk-Othmer Encyclopedia of Chemical Technology.

STYRENE-BUTADIENE RUBBER

Attempts to produce synthetic rubber have been carried out since the 1800s. The introduction of automobiles in the early 1900s gave added impetus to find a substitute for natural rubber, the price of which tripled from \$2.16/kg in 1900 to \$6.73/kg in 1910 (1). The advent of World War I gave Germany incentive to start a crash program on an alternative to natural rubber. From this work, products based on dimethylbutadiene were used, but these were not found to be good substitutes.

In the late 1920s Bayer & Company began reevaluating the emulsion polymerization process of polybutadiene as an improvement over their Buna technology, which was based on sodium as a catalyst. Incorporation of styrene (qv) as a comonomer produced a superior polymer compared to polybutadiene. The product Buna S was the precursor of the single largest-volume polymer produced in the 1990s, emulsion styrene–butadiene rubber (ESBR).

When the United States entered World War II, access to the source of natural rubber was eliminated and the federal government set up a consortium of American rubber manufacturers under the auspices of the Office of Rubber Reserve. A total of 15 styrene–butadiene rubber (SBR) plants were constructed between 1941 and 1942. These plants, devoted to the production of a natural rubber substitute, were run by the four principal rubber companies in the United States: Goodyear, U.S. Rubber, B.F. Goodrich, and Firestone. To increase the number of rubber companies participating in the program, two additional companies were formed from smaller rubber producers: Copolymer Corporation and National Synthetic Rubber Corporation (2). The product agreed upon was called GR-S, an abbreviation for Government Rubber–Styrene, and was based on Buna S. It was the standard general-purpose SBR manufactured until right after World War II, when Germany's work on a low temperature system to generate free radicals for cold emulsion polymerization of SBR became known. The properties of this product were so much better than the hot GR-S that the Office of Rubber Reserve ordered all of the consortium's plants to install refrigeration equipment and begin phasing in the cold-polymerized GR-S. This product has been the basis of the emulsion polymer industry in the United States ever since.

In the mid-1950s, the Nobel Prize-winning work of K. Ziegler and G. Natta introduced anionic initiators which allowed the stereospecific polymerization of isoprene to yield high cis-1,4 structure (3, 4). At almost the same time, another route to stereospecific polymer architecture by organometallic compounds was announced (5).

In the 1960s, anionic polymerized solution SBR (SSBR) began to challenge emulsion SBR in the automotive tire market. Organolithium compounds allow control of the butadiene microstructure, not possible with ESBR. Because this type of chain polymerization takes place without a termination step, an easy synthesis of block polymers is available, whereby glassy (polystyrene) and rubbery (polybutadiene) segments can be combined in the same molecule. These thermoplastic elastomers (TPE) have found use in nontire applications. Styrene–butadiene–styrene blocks are formed by the anionic solution polymerization technique. The long styrene block portion of the polymer chain imparts a rigidity similar to that of vulcanized rubber. Being thermoplastic, the polymers are easily worked on conventional equipment. Also, because the styrene segments soften on heating, the polymer scrap can be reworked, unlike vulcanized rubber.

1. Physical Properties

Desirable properties of elastomers include elasticity, abrasion resistance, tensile strength, elongation, modulus, and processibility. These properties are related to and dependent on the average molecular weight and mol wt distribution, polymer macro- and microstructure, branching, gel (cross-linking), and glass-transition temperature (T_g) (see Elastomers, synthetic).

Emulsion polymerization gives SBR polymer of high molecular weight. Because it is a free-radical-initiated process, the composition of the resultant chains is heterogeneous, with units of styrene and butadiene randomly spaced throughout. Unlike natural rubber, which is polyisoprene of essentially all cis-1,4 configuration, giving an ordered structure and hence crystallinity, ESBR is amorphous. For cold ESBR polymerized at 4–10°C, the typical microstructure of the butadiene portion is 72% trans-1,4, 12% cis-1,4, and 16% 1,2. In hot polymerized ESBR (51.5°C), the typical ratio is changed somewhat to 65% trans-1,4, 18.5% cis-1,4, and 16.5% 1,2 (6).

Unlike SSBR, the microstructure of which can be modified to change the polymer's T_g, the T_g of ESBR can only be changed by a change in ratio of the monomers. Glass-transition temperature is that temperature where a polymer experiences the onset of segmental motion (7).

For ESBR polymerized at 50°C, knowing the percentage of bound styrene in the copolymer allows estimation of the T_g by the following, where S is the weight fraction of the styrene (% bound styrene) (8).

$$T_g\ (^\circ\mathrm{C}) = (-85 + 135\ S)\,/\,(1 - 0.5\ S) \qquad (1)$$

Similarly, for ESBR made at 5°C, the T_g is given by equation 2:

$$T_g\ (^\circ\mathrm{C}) = (-78 + 128\ S)\,/\,(1 - 0.5\ S) \qquad (2)$$

The glass-transition temperaturesfor solution-polymerized SBR as well as ESBR are routinely determined by nuclear magnetic resonance (nmr), differential thermal analysis (dta), or differential scanning calorimetry (dsc).

Among the techniques employed to estimate the average molecular weight distribution of polymers are end-group analysis, dilute solution viscosity, reduction in vapor pressure, ebulliometry, cryoscopy, vapor pressure osmometry, fractionation, hplc, phase distribution chromatography, field flow fractionation, and gel-permeation chromatography (gpc). For routine analysis of SBR polymers, gpc is widely accepted. Table 1 lists a number of physical properties of SBR (random) compared to natural rubber, solution polybutadiene, and SB block copolymer.

Advantages of NR/IR are high resilience and strength, and abrasion-resistance. BR shows low heat buildup in flexing, good resilience, and abrasion-resistance. Random SBR is low in price, wears well, and bonds easily. Block SBR is easily injection-molded, and is not cross-linked. Applications of NR/IR include tires, tubes, belts, bumpers, tubing, gaskets, seals, foamed mattresses, and padding. BR is used in tire treads and mechanical goods, as is random SBR. Block SBR is used in toys, rubber bands, and mechanical goods.

2. Raw Materials

The monomers, butadiene (qv) and styrene (qv), are the most important ingredients in the manufacture of SBR polymers. For ESBR, the largest single material is water; for solution SBR, the solvent.

The quality of the water used in emulsion polymerization has long been known to affect the manufacture of ESBR. Water hardness and other ionic content can directly affect the chemical and mechanical stability of the polymer emulsion (latex). Poor latex stability results in the formation of coagulum in the polymerization stage as well as other parts of the latex handling system.

Table 1. Properties and Applications of Cross-Linked Rubber Compounds[a]

Property	NR/IR[b]	BR[c]	SBR random[d]	SBR block[e]
		Gum stock[f]		
density, g/cm^3	0.93	0.93	0.94	0.94–1.03
tensile strength, MPa[g]	17–21	1.4–7	1.4–2.8	11.7–25.5
resistivity, Ω·cm, log	15–17		15	13
dielectric con-stant at 1 kHz	2.3–3.0	2.3–3.0	3.0	3.4
dissipation factor at 1 kHz	0.0002–0.0003	0.0002–0.0003		
dielectric strength, MV/m[h]				18.9
		Reinforced stock		
tensile strength, MPa[g]	21–28	14–24	14–24	7–21
elongation at break, %	300–700	300–700	300–700	500–1000
hardness, Shore A	20–100	30–100	40–100	40–85
resilience	excellent	excellent	good	excellent
stiffening tem-perature, °C	−30 to −45	−35 to −50	−20 to −45	−50 to −60
brittle tem-perature, °C	−60	−70	−60	−70
continuous high temperature limit, °C	100	100	110	65
		Resistance to solvents and conditions		
acid	good	good	good	good
alkali	good	good	good	good
gasoline and oil	poor	poor	poor	poor
aromatic hydrocarbons	poor	poor	poor	poor
ketones	good	good	good	poor
chlorinated solvents	poor	poor	poor	poor
oxidation	good	good	good	good
ozone	poor	poor	poor	poor
γ-radiation	good	good	good	good

[a] Ref. 9.

[b] *cis*-1,4-Polyisoprene, natural rubber (NR), also made synthetically (IR).

[c] *cis*-1,4-Polybutadiene.

[d] Styrene–butadiene random copolymer, 25 wt % styrene.

[e] Styrene–butadiene block copolymer, $\sim 25\%$ SBR styrene (YSBR).

[f] Cross-linked and unfilled.

[g] To convert MPa to psi, multiply by 145.

[h] To convert MV/m to kV/in., multiply by 25.65.

In converting ESBR latex to the dry rubber form, coagulating chemicals, such as sodium chloride and sulfuric acid, are used to break the latex emulsion. This solution eventually ends up as plant effluent. The polymer crumb must also be washed with water to remove excess acid and salts, which can affect the cure properties and ash content of the polymer. The requirements for large amounts of good-quality fresh water and the handling of the resultant effluent are of utmost importance in the manufacture of ESBR and directly impact on the plant operating costs.

Solution polymerization can use various solvents, primarily aliphatic and aromatic hydrocarbons. The choice of solvent is usually dictated by cost, availability, solvency, toxicity, flammability, and polymer structure. SSBR polymerization depends on recovery and reuse of the solvent for economical operation as well as operation under the air-quality permitting of the local, state, and federal mandates involved.

2.1. Styrene

Commercial manufacture of this commodity monomer depends on ethylbenzene, which is converted by several means to a low purity styrene, subsequently distilled to the pure form. A small percentage of styrene is made from the oxidative process, whereby ethylbenzene is oxidized to a hydroperoxide or alcohol and then dehydrated to styrene. A popular commercial route has been the alkylation of benzene to ethylbenzene, with ethylene, after which the crude ethylbenzene is distilled to give high purity ethylbenzene. The ethylbenzene is directly dehydrogenated to styrene monomer in the vapor phase with steam and appropriate catalysts. Most styrene is manufactured by variations of this process. A variety of catalyst systems are used, based on ferric oxide with other components, including potassium salts, which improve the catalytic activity (10).

In 1990, the annual U.S. capacity to manufacture styrene monomer was 4,273,000 t/yr, and production was 3,636,000 t/yr (11). Polystyrene resin is the dominant user of styrene monomer. SBR use is about 7% of U.S. domestic styrene monomer production. Worldwide production in 1995 was projected to be 77% of capacity as demand increased just under 5% per year, from 1990 consumption of 13,771,000 to 17,000,000 metric tons in 1995.

2.2. Butadiene

Although butadiene was produced in the United States in the early 1920s, it was not until the start of World War II that significant quantities were produced to meet the war effort. A number of processes were investigated as part of the American Synthetic Rubber Program. Catalytic dehydrogenation of *n*-butenes and *n*-butanes (Houdry process) and thermal cracking of petroleum hydrocarbons were chosen (12).

Economic considerations in the 1990s favor recovering butadiene from by-products in the manufacture of ethylene. Butadiene is a by-product in the C4 streams from the cracking process. Depending on the feedstocks used in the production of ethylene, the yield of butadiene varies. For use in polymerization, the butadiene must be purified to 99+%. Crude butadiene is separated from C_3 and C_5 components by distillation. Separation of butadiene from other C_4 constituents is accomplished by salt complexing/solvent extraction. Among the solvents used commercially are acetonitrile, dimethylacetamide, dimethylformamide, and *N*-methylpyrrolidinone (13). Based on the available crude C_4 streams, the worldwide forecasted production is as follows: 1995, 6,712,000; 1996, 6,939,000; 1997, 7,166,000; and 1998, 7,483,000 metric tons (14). As of January 1996, the 1995 actual total was 6,637,000 t.

2.3. Soap

A critical ingredient for emulsion polymerization is the soap (qv), which performs a number of key roles, including production of oil (monomer) in water emulsion, provision of the loci for polymerization (micelle), stabilization of the latex particle, and impartation of characteristics to the finished polymer.

Fatty acid soap was first used for ESBR. Its scarcity prompted the investigation of rosin acids from gum and wood as substitutes (1). The discovery of the disproportionation of rosin allowed rosin acid soaps to overcome the polymerization inhibition of untreated rosin acids. Rosin acid soaps gave the added benefit of tack to the finished polymer. In the 1990s, both fatty acid and rosin acid soaps, mainly derived from tall oil, are used in ESBR.

3. Polymerization

ESBR and SSBR are made from two different addition polymerization techniques: one radical and one ionic. ESBR polymerization is based on free radicals that attack the unsaturation of the monomers, causing addition of monomer units to the end of the polymer chain, whereas the basis for SSBR is by use of ionic initiators.

Free-radical initiation of emulsion copolymers produces a random polymerization in which the trans/cis ratio cannot be controlled. The nature of ESBR free-radical polymerization results in the polymer being heterogeneous, with a broad molecular weight distribution and random copolymer composition. The microstructure is not amenable to manipulation, although the temperature of the polymerization affects the ratio of trans to cis somewhat.

In solution-based polymerization, use of the initiating anionic species allows control over the trans/cis microstructure of the diene portion of the copolymer. In solution SBR, the alkyllithium catalyst allows the 1,2 content to be changed with certain modifying agents such as ethers or amines. The use of anionic initiators to control the molecular weight, molecular weight distribution, and the microstructure of the copolymer has been reviewed (15).

3.1. Emulsion Polymerization

Emulsion SBR was commercialized and produced in quantity while the theory of the mechanism was being debated. Harkins was among the earliest researchers to describe the mechanism (16); others were Mark (17) and Flory (18). The theory of emulsion polymerization kinetics by Smith and Ewart is still valid, for the most part, within the framework of monomers of limited solubility (19). There is general agreement in the modern theory of emulsion polymerization that the process proceeds in three distinct phases, as elucidated by Harkins (20): nucleation (initiation), growth (propagation), and completion (termination).

The nucleation stage for sparingly water-soluble monomers, such as styrene and butadiene, lasts up to 15 to 20% conversion of monomer to polymer. Free radicals from some source initiate polymerization in one of four loci: (*1*) in the water phase where a free radical attacks a soluble monomer molecule (homolytic nucleation); (*2*) at some part of the monomer-swollen micelle (micellar nucleation); (*3*) at the combined surfactant molecule and solvated monomer oligomer in the dispersed phase (nucleation by hydrophobic association); and (*4*) at the surface of the stabilized monomer droplet. In the first case, the growing oligomer reaches a finite chain length and collapses to form a polymer particle. Available soap then stabilizes this particle. For SBR, the most important source of polymer generation is the micelle. Nucleation by hydrophobic association, similar to homogenous nucleation, forms particles as the oligomer chain reaches a finite length and precipitates out of solution as a particle stabilized with a layer of soap. In the fourth case, because the number of monomer droplets is small in relation to the number of available monomer-swollen micelles, polymer formation in the droplet is not statistically significant on account of the great difference in surface area of micelles compared to the monomer droplets and is therefore generally ignored.

The onset of the growth stage is characterized by the disappearance of the micelles. At this point, the growing micelle undergoes a metamorphosis, becoming a polymer particle, now surrounded by a charged layer of surfactant. During this phase, monomer from the shrinking droplets continues to diffuse through the water phase. Polymerization proceeds at a constant rate under steady-state conditions. It is during this stage that free surfactant is made available. The surfactant arises from the following sources: the shrinking monomer droplets, released surfactant from agglomeration of latex particles, and released surfactant from the growing polymer particles which need less surfactant coverage at a larger size because of the surface-to-volume ratio. If enough soap becomes available then more micelles can form. This results in another particle population that gives a bimodal particle distribution. This stage for SBR ends at 55–65% conversion.

The completion stage is identified by the fact that all the monomer has diffused into the growing polymer particles (disappearance of the monomer droplet) and reaction rate drops off precipitously. Because the free radicals that now initiate polymerization in the monomer-swollen latex particle can more readily attack unsaturation of polymer chains, the onset of gel is also characteristic of this third stage. To maintain desirable physical properties of the polymer formed, emulsion SBR is usually terminated just before or at the onset of this stage.

Advantages of emulsion polymerization of SBR include the following: (*1*) high molecular weight polymer at high rates; (*2*) relatively low viscosity of the latex formed to give good heat transfer of the generated exotherm; (*3*) good control of the polymerization temperature; (*4*) ease of removing unreacted monomers and their recovery; and (*5*) ease of processing the finished latex into dry polymer product.

The original emulsion SBR was run at high temperature (50°C) using a fatty acid soap system (Table 2). This was because the available free-radical source was potassium peroxydisulfate, $K_2S_2O_4$, which depends on elevated temperature for the production of free radicals (thermal decomposition). It was found early on that dodecyl mercaptan played a key role in the polymerization initiation, as well as in the regulation of the polymer molecular weight. It was proposed that the mercaptan radical formed from the action of the persulfate radical as the initiating species for polymerization (22). More recently it has been shown that the enhancement of the mercaptan promoting effect is specific to fatty acid soap containing persulfate-initiated diene systems (23).

Originally, the production of emulsion SBR was conducted by the batch method, which involves the charging of the entire recipe ingredients at the same time. As the polymerization advances, the amount of solids (polymer) increases. The percentage of solids is related to the percentage of conversion of monomer to polymer. At the proper conversion rate, in this case 75%, a dilute solution of a chemical called a shortstopping agent is added to the reactor. Hydroquinone, at low levels, is effective. The termination of polymerization is accomplished in two ways. First, shortstopping agents, ie, reducing agents, combine with the initiating species, ie, an oxidizing agent, and effectively destroy the source of free radicals. The second step is to trap and neutralize the free radicals already generated. In the case of hydroquinone, it reduces the persulfate and effectively destroys the generation of any free radicals (24). As it is oxidized to the quinone structure, it becomes an effective free-radical acceptor, scavenging any remaining free radicals.

The shortstopped latex is transferred to one of a series of large vessels, referred to as blowdown tanks, which hold two batches in addition to adequate vapor space. The hot latex is then transferred to large horizontal tanks by pressure differential. These tanks are referred to as flash tanks, for as the latex enters the tank it degasses, that is, releases the residual butadiene, gaseous monomer. The degassed latex is then pumped to the top of a plate column where it is contacted by steam entering the bottom, with the column operating under vacuum. This countercurrent steam distillation of the hot latex efficiently removes the residual styrene monomer. Because SBR contains a high percentage of unsaturation (double bonds) from the butadiene, it is susceptible to degradation by heat, light (uv energy), and O_2 (oxidation). Certain chemicals called antioxidants effectively protect polymers from this degradation. The finished latex containing antioxidant is then subjected to a two-stage coagulation that breaks the emulsion, resulting in a slurry of rubber crumb. The crumb is then passed through a series of washes and dewatering, finally reground and then dried to a low moisture content in large, continuous-belt dryers heated by direct gas-fired burners or steam pipes. The crumb exiting the dryer is then baled in a hydraulic baler in standard 80-lb bales ($\sim$36 kg), bagged or film-wrapped, and boxed for shipment in standardized containers.

Through the years, improvements in the finishing process eliminated the need of two-stage coagulation, ie, creaming the latex with sodium chloride and coagulating this agglomerated latex with sulfuric acid. The same results are achieved by mixing the salt and acid and coagulating in one step. To aid the complete coagulation of the SBR latex, small amounts of coagulant aids are added. These coagulant aids are usually based on polyamines. In the mid-1970s, many commercial ESBR manufacturers replaced the brine (NaCl) by increasing the level of polyamine coagulants. A significant benefit from the change was in the reduction of ash residue in the polymer. Single-screw dewatering presses replaced vacuum filters for effective dewatering of the crumb. The screw dewaterers express large amounts of water at its boiling point as a result of the work put into the

Table 2. Typical SBR Recipes[a]

		Cold SBR	
Elastomer	Hot SBR 1000	1500	1502
Composition, phm			
butadiene	71	71	71
styrene	29	29	29
potassium peroxydisulfate	0.3		
p-menthane hydroperoxide (PMHP)		0.12	0.12
n-dodecyl mercaptan (DDM)	0.5		
t-dodecyl mercaptan (TDM)		0.2	0.18
Emulsifier makeup, phm			
water[b] monomer/water	200	200	200
disproportionated tall oil rosin acid soap	4.5–5	4.5	1.35
hydrogenated tallow fatty acid soap	4.5		3.15
potassium chloride	0.3	0.3	0.3
DARVAN WAQ (secondary emulsifier)		0.1	0.1
Versene Fe-3 (iron complexing agent)		0.01	0.01
sodium dithionate (oxygen scavenger)[c]		0.025	0.025
Sulfoxylate activator makeup, phm			
ferrous sulfate heptahydrate		0.04	0.04
Versene Fe-3		0.06	0.06
sodium formaldehyde sulfoxylate (SFS)		0.06	0.06
Shortstop makeup, phm			
methyl namate	0.05	0.05	0.05
diethylhydroxylamine	0.015	0.015	0.015
Polymerization conditions			
temperature, °C	50	5	5
final conversion, %	72	60–65	60–65
coagulation	acid/amine	acid/amine	acid/amine
antioxidant, ~0.5 – 0.75 on rubber	stainer	stainer	nonstainer
organic acid content, by weight	5–7	5–7	5–7
styrene content, by weight	24	24	24
mooney viscosity ML-4, min at 100°C	48	46–58	46–58

[a] Ref. 21.

[b] Monomer/water ratio adjusted to 1:2.

[c] pH of solution to 10–10.5.

polymer as it passes through the machine. Soluble salts are released with the water, resulting in lower ash content of the polymer. Figures 1 and 2 illustrate a modern production flow sheet for manufacturing solid ESBR.

Initially, all of the SBR polymer known as GR-S produced during World War II was by the batch process. Later, it was thought that a higher volume of polymer would be needed for the war effort. The answer was found in switching from batchwise to continuous production. This was demonstrated in 1944 at the Houston, Texas, synthetic rubber plant operated by The Goodyear Tire & Rubber Company. One line, consisting of 12 reactors, was lined up in a continuous mode, producing GR-S that was more consistent than the batch-produced polymer (25). In addition to increased productivity, improved operation of the recovery of monomers resulted because of increased (20%) reactor capacity as well as consistent operation instead of up and down, as by batchwise polymerization.

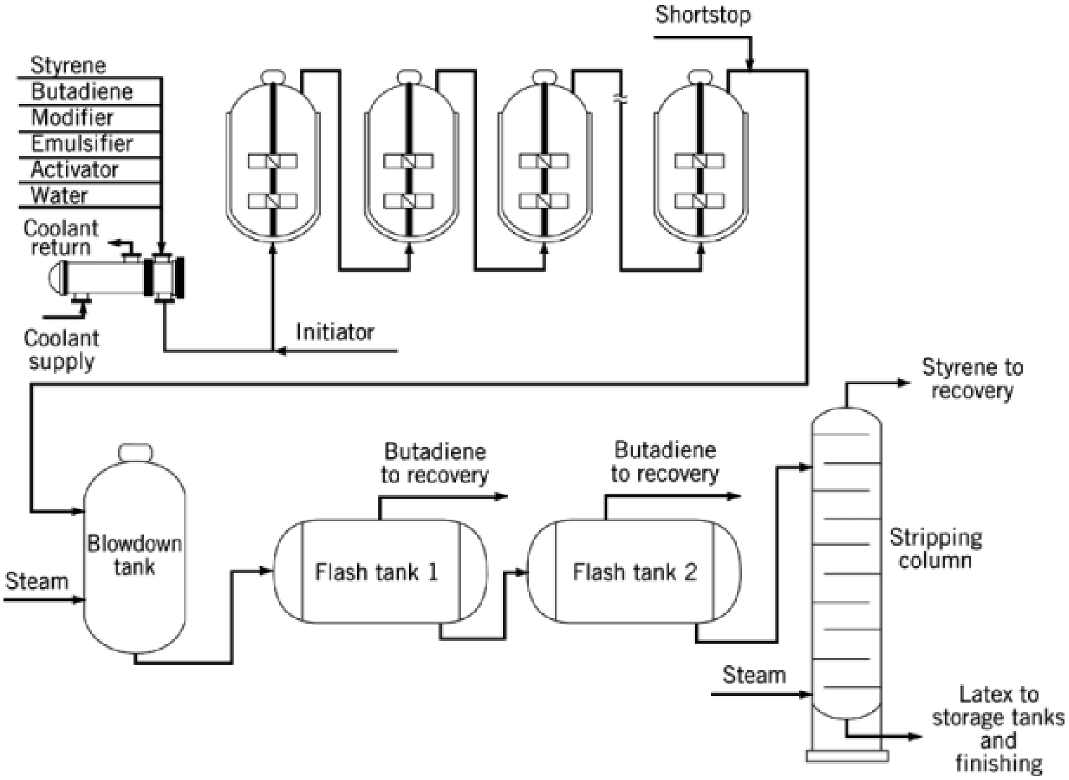

Fig. 1. Typical continuous emulsion SBR polymerization.

Continuous polymerization is accomplished by making up all recipe ingredients in solutions, which are mixed with the monomer streams, brought to desired temperature, and initiated by addition of the free-radical source. Of critical importance is the accurate makeup of the solutions and precise metering of all the streams. Modern ESBR plants depend on computer control (distributive control systems). The reactors are connected in series so that the liquid flow is into the bottom and out the top of each agitated vessel. The residence time in the reactor train is controlled by either a variable volume last reactor or a series of large-diameter pipes (displacement columns), whereby at the correct solids percentage (conversion), the shortstop is added to the exiting latex (see Fig. 1).

After World War II, it was reported that the Germans had been working on a cold emulsion polymerization based on a redox initiation system that gave far superior SBR to the conventional hot polymerization (see Table 2). The principal differences were a polymerization temperature of 5°C instead of 50°C, monomer-to-polymer conversion of 60–65% instead of 75%, and the use of a reduction/oxidation system (redox) to supply free radicals by chemical rather than thermal means. The superiority of cold over hot SBR was attributed, in part, to the greater linearity and less gel of the cold polymer. It was shown that in the cross-linking reaction of butadiene, the ratio of the rate of cross-linking to the rate of propagation is constant up to the point where the monomer phase disappears (26). This ratio decreases as the polymerization temperature is lowered. Thus, there are fewer cross-linking sites at lower temperatures. At the point of monomer depletion (Smith-Ewart third stage), cross-linking increases rapidly. By lowering the conversion rate at which the polymerization is terminated, that point is not reached.

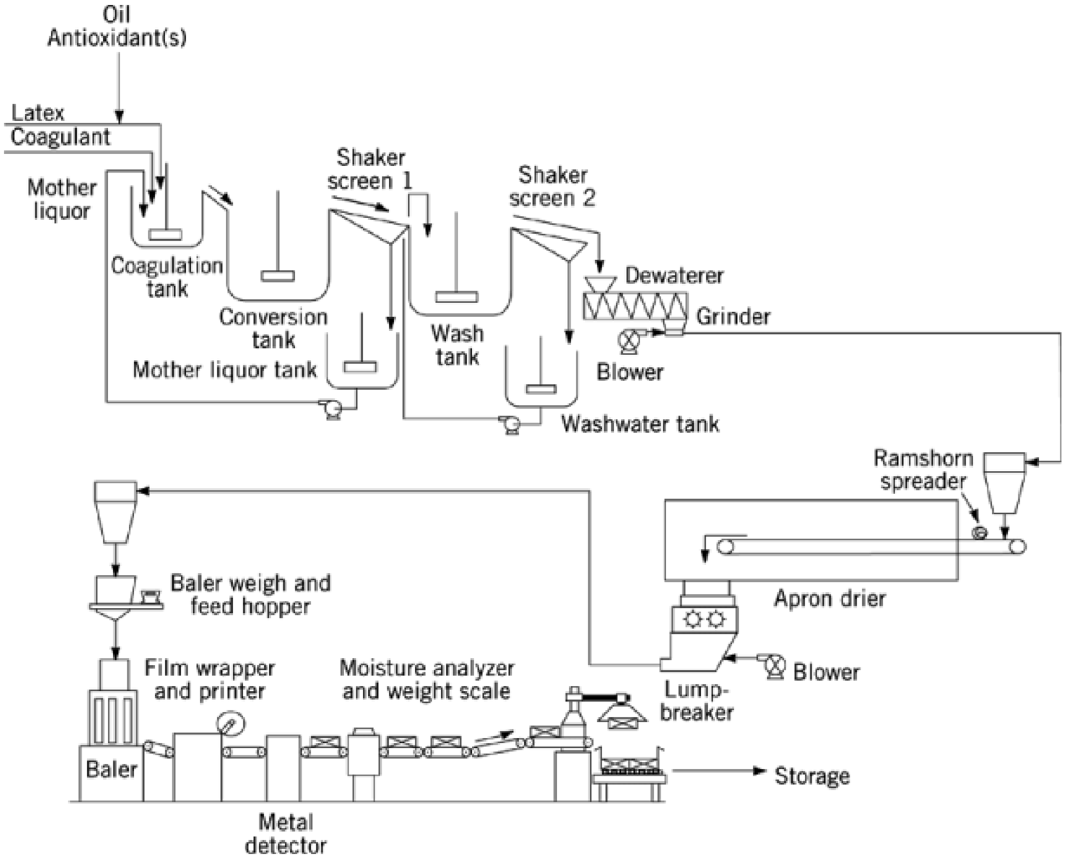

Fig. 2. Typical emulsion SBR finishing.

The impact of cold GR-S was quite pronounced. The U.S. government edicted that all of the emulsion SBR plants switch to the cold process. This required addition of refrigeration capacity in these plants as well as other significant changes, such as insulation of reactors, improved vacuum to reduce oxygen that retards polymerization, and the heating of latex in blowdown tanks to aid in the disengagement of butadiene when transferred to the flash tanks.

It was found that cold emulsion SBR could be made at very high molecular weight, combined with petroleum-based oils at a very high level. Although the polymer could take up oil to the extent of 60 parts of oil per 100 parts of polymer, a standard level of 37.5 parts of oil per 100 parts of polymer was established because the plasticizing power of the oil would require extremely high polymer molecular weight at the 60 part level. The oil was added to the latex as an emulsion and cocoagulated in the standard system. The resultant oil-extended polymer had the benefits of very high molecular weight (improved stress–strain properties) with the processibility of medium Mooney viscosity SBR. Extending pure polymer with oil increased the amount of product over 25%. In addition, the economics of oil-extended SBR was quite attractive considering that a 36-kg bale contained about 10 kg of a low cost process oil.

Several different petroleum process oils are used as extenders for SBR. These are classified as highly aromatic, aromatic, naphthenic, and paraffinic. The highly aromatic oils give the most desirable physical properties to the polymer and are widely used in tire treadstock. However, these oils impart a black color to the polymer and produce staining, ie, discoloration of light-colored articles that come in contact with products containing the oil. For light-colored articles and products in contact with light-colored materials, naphthenic or paraffinic oils are preferred.

The properties of emulsion SBR are comparable to those of natural rubber only when SBR is reinforced with carbon black. Carbon black can be slurried in water and then combined with the SBR latex and cocoagulated to give a product called black masterbatch. The black masterbatch would require considerably less time and energy to get the carbon black dispersed in the nonproductive compound than if it were dry-mixed with the polymer. Other advantages of handling black masterbatch are the elimination of inventorying and handling carbon black, less energy demand in mixing stocks, and better dispersability of the carbon black in the compound.

Black masterbatch can be made with or without oil-extended SBR. Commercially there are available, worldwide, 11 numbered ESBR cold black masterbatches and 15 ESBR cold oil-black masterbatches (27). These types range in black type and content as well as oil type and amount. Of course, not every listed product is available from every supplier.

3.2. Solution SBR

Addition polymerization is accomplished in three steps: initiation, propagation, and termination. The alkyllithium-initiated polymerization in hydrocarbon solvent has no termination step, resulting in living polymer. The mechanism for initiation is thought to be dependant on the addition of the lithium alkyl across the vinyl double bond giving an organolithium compound. Propagation is effected by the further addition of monomer as a stepwise reaction, reforming the same type of carbon–lithium bond (28).

Without the termination step in the alkyllithium polymerization, the batch polymerization results in a copolymer composition of styrene and butadiene that markedly changes with polymer conversion. This produces blockiness, ie, long segments of one constituent in the copolymer chains. An explanation for this behavior is that the butadiene reactivity is considerably greater than that of styrene in the copolymerization and has been shown to be caused by the high cross-propagation rate of the styryllithium anion (29). This mechanism actually allows great flexibility in producing very different types of polymers. The so-called tapered block polymer is made by polymerizing styrene and butadiene monomers with butyllithium as the initiator. By addition of certain chemicals such as ethers, tertiary amines, and phosphites, random distribution of the comonomers is achieved. Certain of these additives also affect the microstructure of the butadiene portion. It is thus possible to control polymer composition, monomer distribution sequence, microstructure (trans-1,4/cis-1,4 ratio constant at variable vinyl level), molecular weight, molecular weight distribution, and polymer chain structure. Figure 3 shows a flow diagram for the continuous production of solution SBR. The kinetics of alkyllithium solution copolymerization of styrene and butadiene in hydrocarbon solvent, along with techniques to randomize the resultant polymer, have been reviewed (30).

Once the ability to control the randomization of solution SBR was understood and established, the commercialized SSBR began to displace some of the ESBR in tire applications. It was found that the SSBR alone could achieve the same desired properties that blends of ESBR and polybutadiene gave, thus simplifying the compound recipes. The combination of low rolling resistance and high wet traction without sacrificing abrasion resistance (tread wear) is attainable with SSBR but not with ESBR alone. Also, by controlling the vinyl microstructure to a low level, a lower T_g is achieved than for ESBR at the same styrene content. This allows for a higher level of oil and carbon black to be added (31).

Because the styrene segments of block copolymers soften on heating, properties that depend on stiffness, hardness, abrasion, etc, may suffer. Conversely, the polymers flow much more readily on molding, extruding, etc. This property allows them to be used in shoe soling and wire insulation applications. Until more recently, the use of block SSBR in tire tread applications was not considered because of the significantly higher running temperature associated with compounds containing them. A Japanese patent claims that the use of a low

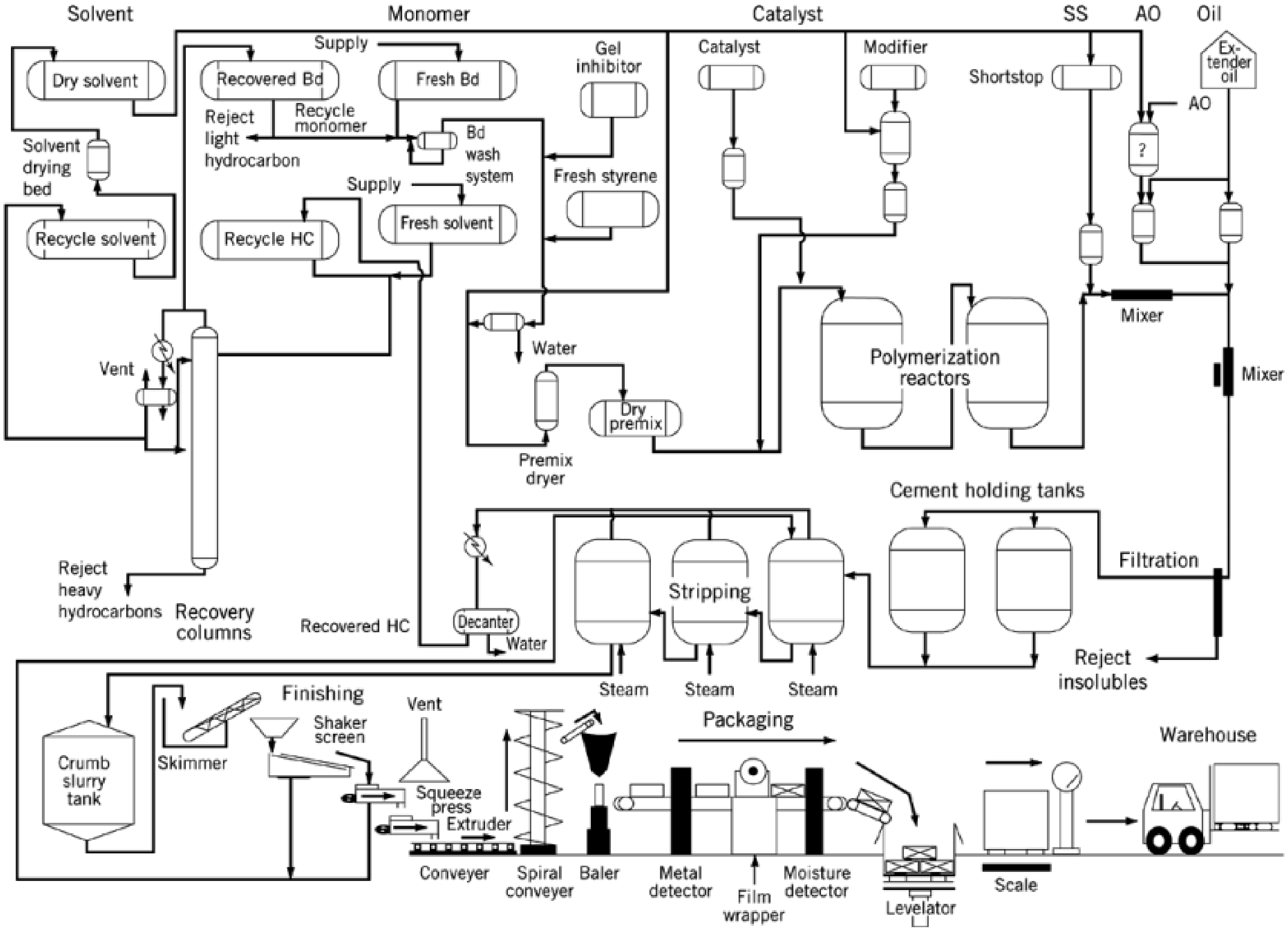

Fig. 3. Solution SBR manufacture by continuous process where Bd=butadiene, HC=hydrocarbon, AO=antioxidant, and SS=shortstop.

molecular weight random block copolymer of styrene and butadiene (A–B–A block SSBR) as part of a tire tread composition imparts improved grip (adhesion) and abrasion resistance to the tire (32).

4. SBR Compounding and Processing

The initial production of GR-S rubber required a learning period in processing before rubber workers were comfortable with the new synthetic rubber. Although softer and more plastic initially, the GR-S did not break down as much as natural rubber. Once familiar with the differences, processing GR-S was handled quite comfortably. The same was true when the cold GR-S was introduced, followed by the oil-extended version, and SSBR.

Development of the Mooney viscometer gave compounders an indication of the processibility of different lots of the uncompounded polymer. This machine measures the torque resistance encountered by a rotor revolving in a chamber surrounded by polymer at a constant temperature. The resulting Mooney number describes the toughness of the polymer and is an indirect measure of molecular weight.

Gel, the insoluble fraction of polymer formed by high conversion of monomer to polymer, excessive mixing, poor antioxidant protection, etc, increases the difficulty of mixing, reduces tensile strength, increases modulus, and decreases the resistance to cut growth. Polymers with significant gel content have reduced elastic memory (but lower shrinkage and lower surface roughness) and improved dimensional stability, two important qualities in extrusion and calendering operation.

Vulcanization was discovered by Goodyear in 1839 (33). By incorporating elemental sulfur with natural rubber and heating the mass, he found that the resultant compound yielded a tough, elastic material, markedly different from the unvulcanized state. Modern rubber compounding (qv) has come a long way since the discovery of vulcanization, but its explanation still remains quite theoretical (34). As a class, SBR is slower curing than natural rubber. This is thought to be caused by the lower unsaturation in SBR.

The art of compounding requires extensive experience and knowledge of the many compound ingredients. A typical rubber compound in addition to polymer contains one or more ingredients from the following general classes: vulcanizing agents, accelerators, accelerator activators, antioxidants, pigments, and softeners (see Rubber chemicals) (35).

The vulcanizing agent, which supplies the bridge between the polymer chains, is still furnished predominantly by the sulfur molecule in commercial formulations. Peroxide vulcanizers that produce carbon-to-carbon cross-links are also important. Thiuram disulfides are used in special applications, such as improved heat resistance. Other agents are of more academic interest.

Accelerators are chemical compounds that increase the rate of cure and improve the physical properties of the compound. As a class, they are as important as the vulcanizing agent itself. Without the accelerator, curing requires hours or even days to achieve acceptable levels. Aldehyde amines, thiocarbamates, thiuram sulfides, guanidines, and thiazoles are all classified as accelerators. By far, the most widely used are the thiazoles, represented by mercaptobenzothiazole (MBT) and benzothiazyl disulfide (MBTS).

Accelerator activators are chemicals required to initiate the acceleration of the curing process. They also improve the polymer compound quality. This class includes zinc oxide (pure) and stearic acid. Other compounds that have been in use are litharge, magnesium oxide, amines, and amine soaps.

Antioxidants (qv) are routinely added to the compounds over and above those contained in the polymer at manufacture. Finished products are subjected to a wide variety of activities causing degradation. Molecules with the propensity to neutralize free radicals by destruction, absorption, or disproportionation can accomplish this phenomenon in different ways. Incorporation of two or more different chemical categories often enhances protection much better (synergism) than the use of higher levels of individual additives. The most popular chemical classes shown to have good antioxidant properties are phenols, phosphites, thioesters, and amines. Because many antioxidant compounds are highly colored, they may tint the finished article. Amines and quinolines have the propensity to stain, that is, to transfer some of the color they impart from the compound in which they are used to a surface in contact with that compound, and are classified as stainers. These characteristics must be kept in mind when choosing the antioxidant system.

Antiozonants (qv) prevent or reduce polymer degradation by the active ozone molecule. Some antioxidant compounds, such as the *para*-phenylenediamines, are excellent as antiozonants (36). The protection by these compounds is thought to be either a reaction with the ozone before it can react with the surface of the rubber or an aid in reuniting chains severed by ozone (37).

Pigments (qv) improve or change polymer properties as well as lower product costs. Reinforcement of SBR by carbon blacks allows this family of polymers to compete with natural rubber (see Carbon, carbon black). It is the most important attribute of the pigment in SBR processing. Two other important groups of pigments are the silicates and silicas. Other materials such as zinc oxide, clays, and calcium carbonate act more as inert fillers to lower the overall compound cost rather than to impart reinforcement. Softeners, ie, plasticizers,

Table 3. Synthetic Rubber Production[a,b], 10^3t

Type[c]	1985	1990	1992	1994	% Change, 1993/1994
SBR					
solid	2284	2398	2358	2433	5.0
latex[d]	289	264	300	299	−2.3
polybutadiene elastomer (BR)	978	1164	1264	1452	5.9
polyisoprene rubber (IR)	110	142	115	111	16.8
chloroprene rubber (CR)	321	306	260	276	15.0
ethylene propylene diene monomer (EPDM)	453	622	617	672	11.3
nitrile rubber (NBR)	213	246	255	277	9.1
others	563	574	606	543[e]	−11.3
Total	5211	5716	5775	6063[e]	4.5

[a] Ref. 40.

[b] Excludes Central Europe, Socialist Countries of Asia, CIS.

[c] For all polymers latices are included, except for SBR where they are shown separately.

[d] Excludes carboxylated latices.

[e] The change reflects a change in the International Institute of Synthetic Rubber Producers (IISRP) reporting base; growth rates not available in 1994.

reinforcing agents, extenders, lubricants, tackifiers, and dispersing aids, are used as processing aids to enhance mixing of uncured stocks and soften cured compounds.

SBR rubber compounds are prepared in two stages: the nonproductive and the productive phases. In the nonproductive phase the compound ingredients are mixed, usually in internal mixers (Banbury). The mixing time is usually short and the compound temperature is in the 160–195°C range. This stock is discharged from the mixer to equipment that allows cooling and a convenient storage form, such as a mill or an extruder/die plate that yields a sheet or pelletized form. Usually the material is coated with a slurry of clay, calcium carbonate, or zinc stearate to prevent self-adhesion.

The productive stock, ie, the curable compound, is made up by mixing the nonproductive stock in the Banbury once more with the curative package (sulfur, accelerators, etc). This time the drop temperature is lower, in the range of 95–112°C. The productive stock is then sheeted or pelletized and coated with the dip coat, cooled, and finally stored, ready for further processing for final fabrication.

5. Economic Aspects and Uses

Styrene–butadiene elastomers, emulsion and solution types combined, are reported to be the largest-volume synthetic rubber, with 28.7% of the world consumption of all synthetic rubber in 1994 (38). This percentage has decreased steadily since 1973 when SBR's market share was 57% (39). The decline has been attributed to the switch to radial tires (longer milage) and the growth of other synthetic polymers, such as polyethylene, polypropylene, polyester, and polystyrene. Since 1985, production of SBR has been flat (Table 3).

Worldwide long-term consumption of SBR is projected to increase 2.5% per year through 1999 (Table 4). SBR is forecast to remain the dominant elastomer of all synthetic polymers in the same time frame. In 1993, use of SBR encompassed the following: tires and tire-related products, including tread rubber, 80%; mechanical goods, 11%; other automotive uses, 6%; and adhesives, chewing gum base, shoe products, flooring, etc, for the remaining 3% (41).

North America has led the world in consumption of SBR and will continue for the rest of the twentieth century. As shown in Table 5, total demand for SBR, including emulsion (solid) and solution (solid), was 852,000

Table 4. Worldwide Long-Term New Rubber Consumption by Elastomer Type[a], 10^3 t

Elastomer	1994	1995[b]	1999[b]
SBR			
solid	2,589	2,774	3,085
latex	400	413	467
carboxylated SBR latex	1,473	1,509	1,670
polybutadiene	1,427	1,541	1,726
ethylene propylene diene monomer (EPDM)	653	679	750
chloroprene rubber (CR)	252	258	293
nitrile rubber (NBR)	319	337	391
other synthetics[c]	1,176	1,369	1,549
Total Central Europe SR	250	268	351
Total Asia CPEC SR	485	519	680
Total synthetics	9,022	9,666	10,962
natural rubber	5,425	5,595	6,264
Total new rubber	14,447	15,289	17,226
synthetic, %	62.4	63.2	63.6

[a] Ref. 40.
[b] 1995 and 1999 values are forecast.
[c] Includes isoprene–isobutyl rubber (IIR), polyisoprene rubber (IR), and other synthetic rubbers (SR).

metric tons in 1994, up from 811,000 metric tons in 1993. Since the early 1990s growth has averaged about 3.2% per year. Projected growth in the near future, based on the tight supply of natural rubber, is 4–5%, through 1999.

6. Health and Safety Factors

Air quality and plant effluent have been monitored and more or less regulated from the inception of SBR manufacture. Between the 1970s and 1990s, regulatory restrictions on plant operations have increased significantly. The ever-decreasing limits on exposure levels include styrene and butadiene monomers as well as their dimers and by-products. Most local and state governments have strict discharge permits that limit what kind of chemicals and how much of it can be emitted into the environment.

The American Conference of Governmental Industrial Hygienists (ACGIH) has set a time-weighted average (TWA) of 50 ppm for styrene monomer (42). For butadiene monomer, ACGIH has set the exposure limit of TWA at 10 ppm (43). As of this writing (1996), the Occupational Safety and Health Administration (OSHA) is reviewing their TWA, which is set at 1000 ppm for butadiene. It is likely that the new TWA will be set at 1 or 2 ppm. Both styrene and butadiene are considered suspect carcinogens.

Title V of the Clean Air Act Amendments of 1990 covers federally approved state operating permits for manufacturing facilities. One requirement of this regulation is that manufacturers must report emissions information of identified hazardous air pollutants specific to their operation from a list of 189 named in the Clean Air Act Amendments. Rubber and tire manufacturers had to meet this requirement by the end of 1995. The Rubber Manufacturers Association has begun an industrywide project to develop accurate and reliable emissions data to aid manufacturers to comply with these requirements (44).

In 1988, the German government issued technical regulation for hazardous materials, TRGS 552. Among other things, 12 volatile nitrosamines were specified and an orientation value of 2.5 μg/m^3 was set for the rubber industry. In 1992 the regulation was redefined. The following levels/action are being enforced in Germany: (*1*) up to 0.1 μg/m^3 constitutes no exposure; (*2*) if levels exceed 0.25 μg/m^3, action needs to be taken; (*3*) if level

Table 5. Worldwide Long-Term New Rubber Consumption by Area and Type[a], 10^3 t

	Western Europe			North America		
Elastomer	1994[b]	1995[c]	1999[c]	1994[b]	1995[c]	1999[c]
SBR						
solid	568	586	620	852	860	883
latex[d]	125	125	125	79	80	83
carboxylated SBR	570	584	645	634	646	699
polybutadiene elastomer (BR)	280	288	312	500	507	510
ethylene propylene diene monomer (EPDM)	225	236	266	264	270	274
chloroprene rubber (CR)	66	66	67	76	77	79
nitrile rubber (NBR) (solid and latex)	89	92	100	122	124	125
other synthetics[e]	241	251	278	408	420	426
Total synthetic rubber	2164	2228	2413	2935	2984	3080
natural rubber	900	930	1010	1106	1111	1103
Total new rubber	3064	3159	3423	4041	4094	4183
synthetic, %	70.6	70.5	70.5	72.6	72.9	73.6
thermoplastic elastomer (TPE)	299	314	371	358	387	496

[a] Ref. 40.
[b] Estimated December 1994.
[c] Forecast prepared during first quarter of 1995.
[d] Noncarboxylated.
[e] Includes isoprene–isobutyl rubber (IIR), polyisoprene rubber (IR), and others.

Table 6. (*Continued*)

Asia and Oceania			Africa and Middle East		
1994[b]	1995[c]	1999[c]	1994[b]	1995[c]	1999[c]
684	714	832	60.7	63.2	71.5
141	146	164	4.0	4.1	6.0
231	241	280			
445	464	540	28.0	28.7	31.5
141	146	165	5.0	5.3	7.0
84	87	101	6.0	6.1	6.5
77	80	94	3.2	3.2	3.7
217	227	267	21.0	21.8	25.0
2020	2105	2443	127.9	132.5	151.3
2070	2120	2340	188.0	194.9	215.2
4090	4224	4783	315.8	327.4	366.5
49.4	49.8	51.0	40.5	40.5	41.3
148	154	179	5.5	5.9	7.7

exceeds 0.65 μg/m^3, respirators and medical monitoring must be offered; and (*4*) if levels exceed 1.00 μg/m^3, respirators are mandatory.

This regulation is only concerned with volatile nitrosamines in the workplace air. A principal problem in enforcement is in the detection method. Only certain analytical laboratories are certified and reproducibility is difficult to achieve. Epidemiological studies have shown volatile nitrosamines to be carcinogenic in animals (45). Volatile nitrosamines are formed when secondary amine compounds break down and are nitrosated. In rubber this occurs primarily during the vulcanization stage, where accelerators, which are predominantly secondary amine compounds, decompose, forming lower molecular weight compounds, and are nitrosated either from oxides of nitrogen in the air or from nitrate–nitrite salts in the vulcanization process. Other sources of these secondary amines are as contaminants in compounding ingredients and as trace amounts in emulsion SBR, from the residue of certain shortstopping chemicals used in its manufacture.

There is an industry trend to supply SBR certifiably free of volatile nitrosamines or nitrosatable compounds. This has generally been accomplished by replacing shortstop systems based on carbamates and hydroxyl amines with products that are not based on secondary amines or are secondary amines of high molecular weight, such as dibenzyldithiocarbamate. A more recently issued patent for ESBR shortstop is based on isopropylhydroxylamine, a primary amine that does not form nitrosamine (46).

Of primary concern to local, state, and federal governments is the growing stockpile of scrap tires. It was estimated by the Rubber Manufacturer's Association that for the year 1994, 242 million tires were added to the staggering number stockpiled haphazardly throughout the United States. The threat of huge piles of scrap tires catching fire is cited as a principal concern. Past experience has shown how such fires pollute the air and threaten groundwater as the large quantities of oil released in the incomplete burning become a serious runoff problem. In 1991 the federal government instituted the Intermodal Surface Transportation Act, which, among other things, mandates the use of ground rubber from scrap tires in asphalt paving. Being an unfunded mandate, it was ignored by most states and the Federal Highway Administration has not been authorized money to enforce this provision (47). There is heated debate on whether or not this technology is in fact worthwhile (48). Although use of scrap tires is projected to increase rapidly in the next three to five years, the only economically feasible use has been as a fuel or fuel supplement in utility and industrial applications (see Recycling, rubber) (49).

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Styrene; Styrene plastics; Elastomers, synthetic