

Production process for halobutyl rubber

The invention relates to a method for producing halobutyl rubber by copolymerising isobutyl and isoprene in a solvent to butyl rubber, whereby the solvent may not be dissolvable during a suspension method (for example, chloromethane) or during a solution process (for example, isopentane, pentane, hexane), and subsequent halogenation of the butyl rubber, as well as a device for this.

Description of state of the art

The production of halobutyl rubber is a continuous two-stage process. First, copolymerisation is carried out to obtain butyl rubber, then halogenation of the butyl rubber to obtain halobutyl rubber. It all occurs continuously.

The copolymerisation process of butyl rubber is described in Ullmann's Encyclopedia of Industrial Chemistry, 5ed, vol. A23, p. 290, 1993. Copolymerisation includes two monomers (isobutylene and isoprene) and a catalyst / co-catalyst, all of which is dissolved in a solvent. The solvent may be one which is non-soluble for a suspension process (for example, chloromethane), or a soluble solvent for a solution process (for example, isopentane, pentane, hexane or others). It is also possible to start with a suspension process in a tank reactor or in a series of tank reactors, and replace a non-soluble agent with a soluble agent to obtain the

dissolved polymer particles for the next step.

In principle, a suspension or a very aqueous solution must be reached in the tank reactor, in order to avoid a high viscosity. The reaction temperature ranges from -100°C to -30°C. The amount of solvent can amount to 80% or above.

In EP 0 209 253, a copolymerisation process is described in a kneading reactor in an almost solid phase or pasty phase with little solvent (29%) compared to the method described above (about 80% or more). The reaction temperature is -45°C. A final step devolatilises the butyl rubber.

The halogenation of butyl rubber is described in the same encyclopaedia on page 316. The reaction takes place in a tank reactor or in a series of tank reactors. There, extruder halogenation is also described on page 317, where a bulk phase is brought into contact with chlorine or bromine (R.C. Kowalski, Chem. Eng. Prog. 85 (1989) no. 5, 67). Substantially free of water, hydrohalic acids are formed as by-products, not separated and removed by degassing, through which the need for a dispersed phase neutralisation is avoided. The acids do not dissociate, preventing corrosion of the system. Therefore, costly construction material, such as hastelloy, inconel or titanium is avoided.

In US 4,650,832 (Kowalski et.al., 1985) an extrusion process is described, to carry out halogenation during the concentrated phase, resulting in substantial reduction in capital investment. The solution concentration is 5% to 10% and the reaction temperature is 100°C to 120°C. The absence of water, or a dry halogenation process showed no evidence of corrosion after the test runs.

Task

The aim of the present invention is to simplify the entire production process for halobutyl rubber, to make the process safer, to limit the investment costs and produce competitiveness, through fully-automated and flexibly continuous (co)polymers, which can be treated in a continuous process.

Solution

In order to solve the issue, halogenation shall at least occur using a halogenating agent, in particular with chlorine or bromine, in a halogenation kneader.

Such devices are also referred to as mixing kneaders. They serve very diverse purposes. First, evaporation using solvent recovery should be mentioned, which occurs in batches or continually and often in a vacuum. This, for example, enables the treatment of distillation residues and in particular toluene diisocyanate, but also treatment of production residues with toxic or high-boiling solvents in chemical and pharmaceutical production, washing solutions and paint residues, polymer solutions, elastomer solutions from solvent polymerisation, adhesive and sealants.

In a mixing kneader, a polycondensation reaction can take place - usually continuously and in the melt - and is mainly used in the treatment of polyamides, polyesters, polyacetates, polyimides, thermoplastics, elastomers, silicones, urea resins, phenolic resins, detergents and fertilisers. For example, the application takes place on polymer melts following mass polymerisation of the derivatives of methacrylic acid.

A polymerisation reaction can also take place - usually also continually. This is applied to polyacrylates, hydrogels, polyols, thermoplastic polymers, elastomers, syndiotactic polystyrene and polyacrylamides.

In mixing kneader, degassing and/or devolatilisation can occur. This is applied to the polymer melt, after (co)polymerisation of (a) monomer(s), after condensation of polyester or polyamide melts, to spinning solutions for synthetic fibres and to the polymer or elastomer granules or powders in a solid state.

Essentially, single-shaft and twin-shaft mixing kneaders are distinguished. For example, a single-shaft kneader is known from AT 334 328, CH 658 798 A5 or CH 686 406 A5. Hereby, an axial shaft with disc elements, around a rotational axis, in a one-directionally rotating shaft is in housing. This causes the transport of the product in the transport direction. Between the disc elements, counter elements are firmly attached to the housing. The disc elements are arranged in planes

perpendicular to the kneading shaft and form free sectors between them, which shape with the planes of the neighbouring kneading chambers of the disc elements.

A multi-shaft mixing and kneading machine is described in CH-A 506 322. There, there are radial disk elements and axially aligned kneading bars between the discs, arranged on one shaft. Between these discs, frame-like mixing and kneading elements mesh from another shaft. These mixing and kneading elements clean the discs and kneading bars of the first shaft. The kneading bars on both shafts in turn clean the housing's inner wall.

These known twin-shaft kneader mixers, have the disadvantage that they display a weakness due to the eight-shaped housing section in the area of connection of the two shaft housings. In this area, high voltages - that can only be controlled by complicated constructive measures - arise during the processing of tougher products and/or processes that occur under pressure.

A mixing kneader of the abovementioned type is known, for example from EP 0 517 068 B1. In that example, in one mixer housing, two axially parallel shafts rotate either in opposite directions or the same direction. At the same time, mixing bars attached to disc elements work together. In addition to mixing, the mixing bars also have the task of cleaning the surfaces of the mixer housing, shafts and disc elements that come into contact with the product as well as possible, thereby avoiding unmixed zones. Especially in the case of extremely compacting, hardening and encrusting products, the wall effect of the mixing bars leads to high local mechanical strain on the mixing bars and shafts. These force peaks occur in particular when the mixing bars operate in those areas where the product cannot escape easily. Such zones are, for example, occur where the disc elements sit on the shaft.

Furthermore, a mixing kneader of the abovementioned type is known from DE 199 40 521 A1, where the supporting elements in the area of the kneading bars form a recess, so that the kneading bars have the greatest possible axial extension. Such a mixing kneader has an excellent self-cleaning capacity of all the housing and

shaft surfaces that come into contact with the product, but displays the property, that the supporting elements of the kneading bars are required due to the paths of the kneading recesses, which leads to complicated supporting-element forms. Firstly, this results in an expensive production method and secondly, in local voltage spikes on the shaft and the supporting elements in the case of mechanical stress. These voltage spikes - which mainly occur in the sharp-edged recesses and changes in thickness, especially in the area where the supporting elements are welded to the shaft core - are triggers for cracks in the shaft and the supporting elements due to material fatigue.

In order to simplify the two-stage process described above, the kneading technology can be combined with part of the existing process or can be based completely and solely on the kneading technology. The aim is to limit investment costs and to obtain a competitiveness through fully-automated and flexibly continuous (co)polymers, that are treated in a continuous process, at a low shear rate (below 400 s^{-1}) and at low temperatures ($< -30^{\circ}\text{C}$, $< -10^{\circ}\text{C}$, $< -50^{\circ}\text{C}$ for copolymerisation and $< 180^{\circ}\text{C}$, $< 120^{\circ}\text{C}$, $< 100^{\circ}\text{C}$ for dry halogenation) under inert conditions. A steam stripper in the halogenation process stage is completely avoided.

Note: a kneader is a reactor between a tank reactor (limited viscosity) and an extruder (limited residence time, a maximum of 2 minutes). Thus, a mixing kneader can treat products within a period of time/residence time from 8 to 60 minutes or even 120 minutes, in a concentrated phase or nearly solid phase, or in a pasty phase or highly viscous phase, similar to a honey phase, or even in a much higher concentrated phase than honey. A molten (co)polymer or one (a copolymer) above its melting point or above its glass transition temperature can be considered a highly viscous phase or a pasty phase. A paste-like or concentrated polymer phase can be compared to chewing gum which is masticated between human teeth. A self-cleaning, continuous kneader has kneading/conveyor elements that can be compared to human teeth, that masticate and transport chewing gum for a chewing gum mass from an input area to a discharge area.

A single- or twin-shaft discharging device is arranged at the end of the continuous kneader to transport the polymer into the suction area of an optional gear pump. The gear pump places the molten polymer under pressure in a heated transfer tube, to transfer it into the following kneader or in a continuous flow device. The heated transfer tube may be equipped with static mixers. Such a heated transfer tube may also be regarded as a heat exchanger, to raise the polymer temperature. In all of the following figures a discharge gear pump and heat transfer tube are arranged between two continuous flow devices. However, it should be clarified that they are optional and optionally, a heated transfer tube may also be a heat exchanger, in order to increase the product temperature.

Chlorine Cl_2 or bromine Br_2 are described in the figures. However, new or different halogenating agents may also be added instead of chlorine or bromine. If present $\text{Cl}_2/\text{N}_2/\text{s}$ is written, it is understood that chlorine is dissolved in nitrogen, or in a solvent. The same applies to $\text{Br}_2/\text{N}_2/\text{s}$.

Solvents may refer to isopentane, pentane, hexane or alkane, or organic solvents. When a non-soluble agent, such as chloromethane, is referred to, a non-solvent is meant, to maintain the polymer particles in suspension, to form a suspension below the glass transition temperature of the copolymer (-70°C). It may also refer to other non-solvents.

At the end of the process the halobutyl rubber is treated with an optional stripping agent, such as water. Optionally, the water may contain some neutralising substances, to neutralise traces of acidic by-products. The mixing kneaders are shown in the figures with a horizontal housing and a dome, which is arranged vertically on it. If only one dome is shown in the figures, it should nevertheless be understood that two or three domes are possible.

Each kneader can hold additives and/or stabilisers in gaseous, liquid or solid form. In order to add solid additives into a kneader, a single or twin-shaft device is used to cause a continuous supply of powder into the continuous kneader (single or

twin-shaft kneader). A nitrogen purging agent can also be used in the single or twin-shaft feeding device, to prevent air or moisture that may enter the system. Each addition to a kneader can occur at one or more feeding points.

The solvent technology is shown in only one tank, but it may also be a series of tanks.

The drives of the continuous flow devices may be electric or hydraulic.

Whenever degassing is described, it should be understood that a pre-concentration stage can be optionally included, prior to a main evaporator. Such a pre-concentration stage is required if the polymer is very dissolved in a solvent or in its monomers. A pre-concentration stage may comprise a flash drum with a discharging gear pump and with or without a pre-heater, and with or without a loop-back in the pre-heater, or a film degasser with or without a discharging gear pump and with or without a pre-heater. The construction material may be hasteloy, inconel, duplex, titanium, inox or carbon steel.

The invention can be divided into three groups:

Group 1 comprises the existing suspension copolymerisation process in a tank reactor. The continuous halogenation in a concentrated phase or dry halogenation is newly grafted from the existing suspension copolymerisation process.

In a first embodiment, the known suspension copolymerisation process in the tank reactor, chlorobutyl rubber is delivered in a continuous mixer for dry halogenation in a concentrated phase. Solvent can be added to adjust the polymer concentration, to reduce mechanical heat input and avoid granulation between the kneading elements. Addition of the solvent at multiple feeding points is an effective way to expel acidic by-products, HCl or HBr, so that there is dry chlorination to produce chlorobutyl rubber ClIR or dry bromination to produce bromobutyl rubber BIIR. In the final step, traces will be removed from volatile components. Optionally, water may be used as a stripping agent, which is added at multiple feeding points.

A second embodiment shows a similar continuous process, in which the previously state of the art extruder is replaced by a kneader, to remove the remaining volatile components at low shear rates and low temperatures, to avoid or reduce polymer degradation/cross-linking. The water contained in the polymer, effectively drives out the residual monomers.

In a third embodiment, the known suspension is continuously dissolved in one or more tanks in a series, in hot solvent (a non-solvent is replaced by a solvent). This solvent may be hexane or another solvent. The dissolved copolymer is then optionally pre-concentrated before it is placed into the first kneader for the main evaporation, in which a mechanical heat input degasses the solvent and residual monomers/non-solvent. A second kneader removes the remaining volatile components. Dry halogenation follows according to the first embodiment. If the second kneader is omitted, a lesser removal of solvents occurs before dry halogenation. This happens especially if there is concern of granulation, if solvent escapes at such low temperatures. A kneader, which is compacted, is preferred. 5% to 10% of solvent is needed to ensure a stable paste-like phase at a low temperature.

In a fourth embodiment, a known suspension is continuously dissolved in one or more kneaders in series, in hot solvent (a non-solvent is replaced by a solvent). The solvent may be hexane or another solvent. The kneader may provide mechanical heat to degas the non-solvent and helps to mix the small amount of solvent into the polymer matrix. As an optional final stage, a second kneader may be used to remove residual volatile materials. Dry halogenation takes place as described above.

Group 2 refers to the known solvent-copolymerisation process in a tank reactor. Continuous halogenation in a concentrated phase or dry phase halogenation is newly added to this known solvent-copolymerisation process.

The embodiments are similar to those in group 1, however the known solution-copolymerisation process in the tank reactor is connected to a degassing step in a kneader. This results in mechanical heat input, to degas the main component of solvent and residual monomers. As an optional final stage, a second kneader may be used, to remove the remaining liquid components. The optional final stage may be omitted to avoid a granulation of the copolymer at a low temperature. Dry halogenation follows as known.

Group 3 relates to a new continuous, concentrated solvent or bulk copolymerisation process in a kneading reactor, combined with the continuous dry halogenation in the concentrated phase.

In a first embodiment, the copolymerisation of isobutylene and isoprene is accomplished in a continuous kneader in a concentrated phase. The discharged copolymer receives an optional final treatment in a second kneader, to remove the remaining volatile components. Dry halogenation occurs as usual.

A second embodiment is carried out without the optional final stage, to avoid granulation at a low temperature prior to the usual dry halogenation. Residual monomers are optionally expelled at the end of the kneading reactor by adding solvent at several feeding points. Optional back-mixing kneader elements around the centre of the kneading reactor may be helpful to plug the gas compartment between the reaction zone and the stripping zone. An alternative to the optional back-mixing element could include a static, inner baffle plate. Dry halogenation follows as usual.

In a final embodiment, polymerisation and halogenation is carried out in a mixing kneader. Back-mixing kneading elements around the centre of the kneader may be useful to plug the space between the polymerisation and dry halogenation zones. An alternative to the optional back-mixing elements could include a static, inner baffle plate. This method uses a mixing kneader to carry out copolymerisation at a low temperature and also halogenation at a higher temperature, where mechanical heat input is used. Another final stage with an

optional stripping agent removes the remaining volatile materials. Water is a possible example. Various neutralising agents could be added to the water to neutralise acidic residual materials. Additives/stabilisers can be used in the kneading reactor, as well as in the final stage.

Description of figures

Further advantages, features and details of the invention are clarified in the following description of preferred embodiments and through the drawing; this shows in

Figure 1 a block diagram of the inventive method with suspension and extruders stripped with water in the first part;

Figure 2 a block diagram of another embodiment of the inventive method according to figure 1, where an extruder is replaced by a kneader;

Figure 3 a block diagram of another embodiment of the inventive method according to figure 2, where however, the suspension is dissolved in a solvent in a tank reactor;

Figure 4 a block diagram of another embodiment of the inventive method according to figure 3, but without a tank reactor;

Figure 5 a block diagram of another embodiment of the inventive method based on a solution/ bulk copolymerisation in a kneading reactor;

Figure 6 a block diagram of another embodiment of the inventive method with a solution/ bulk copolymerisation and pre-concentration in a kneading reactor;

Figure 7 a block diagram of another embodiment of the inventive method with copolymerisation and halogenation in a kneading reactor.

According to figure 1 and according to the state of the art - as described in Ullmann's Encyclopedia of Industrial Chemistry, 5ed Vol. A23, p.290, 1993 - the two monomers for the production of butyl rubber (isobutyl and isoprene) are added to the reactor (1), in conjunction with a solvent for the polymerisation. A catalyst or co-catalyst can be added at 2. In the case of the solvent for a suspension process, this may refer to a non-soluble solvent (for example, chloromethane), or a soluble solvent for a solution process (for example, isopentane, pentane, hexane, or similar).

The butyl rubber produced this way passes from the polymerisation reactor (1) into two consecutive tanks (4.1 and 4.2), in which a certain amount of solvent can be removed (5).

From tank 4.2, the butyl rubber passes through two extruders (6.1 and 6.2) and is then added to the halogenation kneaders (7) for halogenation, according to the invention method. In the halogenation kneaders (7), a halogenating agent (8) is added to the front area - for example, chlorine dissolved in nitrogen in a solvent or bromine dissolved in a solution. However, these are only examples.

In the halogenation kneaders (7), dry halogenation occurs continuously in the concentrated phase. At 9, a solvent is added - preferably at several feeding points distributed along the length of the halogenation kneader (7). Using this solvent, the polymer concentration in the halogenation kneaders (7) can be adjusted, the mechanical heat input can be reduced and granulation can be avoided by kneading elements.

From the halogenation kneader (7), acidic by-products are removed using a vapour dome (10) and a discharging device (21). If the halogenation occurs using chlorine, the acidic by-product refers to HCl and nitrogen (if applicable); if halogenation occurs using bromine, the acidic by-product refers to HBr and nitrogen (if applicable). Additional nitrogen (11) may also be added to the halogenation kneaders (7).

The halogenated mass (halobutyl rubber) is transferred via a discharge element (12) and a gear pump (13) and added to a final-stage kneader (14). In the final-stage kneader (14), removal of residues of volatile components occurs, at which point water is added (15) as a preferred stripping agent. Here, addition of water also occurs at several feeding points distributed along the length of the final-stage kneader (14).

The gear pump (13) places the molten polymer under pressure in a heated transfer tube (45) in order to put it in the following kneader or in a continuous flow device. The heated transfer tube may be equipped with static mixers. Such a heated transfer tube may also be regarded as a heat exchanger to raise the polymer temperature. In all of the following figures, a discharge gear pump and heat transfer tube are situated between two continuous flow devices. However, it should be clarified that they are optional and a heated transfer tube may optionally also be

a heat exchanger, in order to raise the product temperature.

The volatile components of the water are also discharged (23) via vapour domes (22). The final product is now removed via a further discharging element (16) and a gear pump (17) from the final-stage kneader (14) and can be processed into pellets.

In contrast to the embodiment according to figure 1, in the embodiment according to figure 2 the second extruder (6.2) is replaced by a pre-concentration kneader (18). Via this pre-concentration kneader (18), residual liquid components are removed at a low shear rate and at a low temperature, in order to avoid or reduce polymer degradation/cross-linking. The existing water in butyl rubber and the residual monomers are discharged (20) via a vapour dome (19). Removal of the residual monomers occurs very efficiently via the water, which still contains the polymer.

Another discharging device (24) is connected at the pre-concentration kneader (18), which in turn is connected to a gear pump (25).

According to the embodiment of the present invention and according to figure 3, the two tanks (4.1 and 4.2) are replaced by a solvent tank (26), which is followed by two other pre-concentration kneaders (18.1 and 18.2). After the tank (3) the mass is placed in the solvent tank (26) containing a hot solvent, preferably hexane. In this solvent tank (26), volatile chloromethane or volatile residual monomers are removed (27).

The dissolved copolymer (the butyl rubber) is then placed in the pre-concentration kneaders (18.1 and 18.2), where in each case discharge (20.1 or 20.2) occurs via vapour domes (19.1 and 19.2) for hexane/chloromethane and residual monomers, before the mass is transported into the halogenation kneaders (7). The corresponding discharge devices (24.1 and 24.2) and gear pumps (25.1 and 25.2) are then provided for the respective pre-concentration kneaders (18.1 and 18.2).

In a further embodiment (not shown) of the present invention, the second pre-concentration kneader (18.2) is omitted. This happens especially if there is a risk of

granulation in pre-concentration kneaders, when the solvent disappears at such low temperatures. A 5 to 10% solution is usually required to ensure a safe pasty phase at low temperatures.

According to the embodiment of the invention in figure 4, the solvent tank (26) can be omitted, whereby butyl rubber is added from the polymerisation reactor (3) directly to a pre-concentration kneader (8.3). In this case, hot hexane is added (28) - possibly via several feeding points distributed along the length of the kneader (18.3). Discharge (20.3) of residual monomers and chloromethane then occurs via a vapour dome (19.3).

Also in this embodiment, it is possible to omit the second pre-concentration kneader (18.2) and to add the mass from the pre-concentration kneader (18.3) directly to the halogenation kneader (7).

According to the embodiment of the invention in figure 5, the monomers and solvent are added at 1, and the catalysts/co-catalysts and solvent are added at 2 directly into a copolymerisation kneader (29). After this, copolymerisation occurs continuously in this kneader. Resulting vapours are removed via a vapour dome (30) and a discharging device (31).

The polymer then passes optimally into the pre-concentration kneaders (18) via a discharging device (32) and a gear pump (33) and from there into the halogenation kneader (7).

The embodiment of the present invention according to figure 6 differs from that of figure 5, in that pre-concentration occurs in the same kneader as the copolymerisation. This combination kneader (34) is divided into two zones (35 and 36). In zone 35, copolymerisation takes place; in zone 36 pre-concentration takes place.

Preferably, zones 35 and 36 are separate from each other, which can be achieved using any methods or devices. Primarily, it is intended that the kneading elements inside of the combination kneader are designed so that back-mixing occurs

approximately at the centre of zone (37), resulting in a certain plug formation, so that zones 35 and 36 are thus separated. Alternatively, mechanical plug formation may occur - for example, a dam or weir.

In the combination kneader (34) the addition of nitrogen at 38 is possible.

The pre-concentrated product is transported to the halogenation kneaders (7) via a further discharging device (39) and a gear pump (40).

According to the last embodiment, according to figure 7, copolymerisation and halogenation occur in a combination kneader (41). Here, the copolymerisation zone (35) is separated from the halogenation zone (42) via a plug zone (37). According to figure 6 the monomers plus solvent are added to the copolymerisation zone (35) at 1, and the catalyst/co-catalyst and optionally a solvent are added at 2. The corresponding vapours are removed via a vapour dome (43).

After copolymerisation, the polymer is transferred to the Halogenation zone (42), where the halogenating agent is added (8). In both zones (9.1 and 9.2) a solvent - and optionally nitrogen (38) - is also added to adjust the concentration. A further vapour dome (44) provides discharge (21) of acidic by-products, solvent and nitrogen.

List of references

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List of reference numbers

1	Monomers + chloromethane	34	Combination kneader	67	
2	Catalyst	35	Copolymerisation zone	68	
3	Polymerisation reactor	36	Pre-concentration zone	69	
4	Tank	37	Plug zone	70	
5	Discharge	38	Nitrogen	71	
6	Extruder	39	Discharging device	72	
7	Halogenation Kneader	40	Gear pump	73	
8	Halogenating agent	41	Combination kneader	74	
9	Solvent	42	Halogenation zone	75	
10	Vapour dome	43	Vapour dome	76	
11	Nitrogen	44	Vapour dome	77	
12	Discharging device	45	Transfer tube	78	
13	Gear pump	46		79	
14	Final-stage kneader	47			
15	Water inlet	48			
16	Discharging device	49			
17	Gear pump	50			
18	Pre-concentration Kneader	51			
19	Vapour dome	52			
20	Discharge	53			
21	Discharging device	54			
22	Vapour dome	55			
23	Discharge	56			
24	Discharging device	57			
25	Gear pump	58			
26	Solvent tank	59			
27	Discharge	60			
28	Inlet	61			
29	Copolymerisation Kneader	62			
30	Vapour dome	63			
31	Discharge	64			
32	Discharging device	65			
33	Gear pump	66			

Claims

1. A method for producing halobutyl rubber by copolymerising isobutyl and isoprene in a solvent to butyl rubber, whereby the solvent may not be dissolvent for a suspension method (for example, chloromethane) or being dissolvent for a solution process (for example, isopentane, pentane, hexane), and subsequently halogenation of the butyl rubber, characterised by halogenation at least occurring using a halogenating agent (8), especially with chlorine or bromine, in a halogenation kneader (7).
2. A process according to claim 1, characterised by pre-concentration of the butyl rubber prior to halogenation for dry halogenation.
3. A process according to claim 1 or 2, characterised by addition of solvent to the halogenation kneader (7) to adjust the polymer concentration, to cool and to avoid granulation.
4. A process according to claim 3, characterised by addition of solvent (9) to the halogenation kneader (7) at several points distributed along the length.
5. A process according to at least one of the above mentioned claims, characterised by the addition of nitrogen (11) or another inert gas to the halogenation kneader (7).
6. A process according to at least one of the above mentioned claims, characterised by addition of the halogenating agent (8) to the front area of the halogenation kneader (7) and removal of solvent vapours and possible acidic by-products (21), especially HCl and HBr, produced in the halogenation kneader (7).
7. A process according to at least one of the above mentioned claims, characterised by a further, final treatment of the product following halogenation, in a final-stage kneader.

8. A process according to claim 7, characterised by stripping of the product in the final-stage kneader (14) with water (15), which is added to the final-stage kneader (14) at several points distributed along the length.
9. A process according to at least one of the above mentioned claims, characterised by halogenation preceded by a pre-concentration kneader (18), in which, particularly water, solvent and/or residual monomer (20) is removed from the butyl rubber.
10. A process according to at least one of the above mentioned claims, characterised by placing the butyl rubber in a solvent prior to halogenation and removing this prior to halogenation.
11. A process according to claim 10, characterised by mixing of the butyl rubber in a solvent tank (26) and/or pre-concentration kneader (18.3) with hot solvent.
12. A process according to claim 11, in which the solvent tank (26) is at least followed by a pre-concentration kneader (18.1), in which the product is concentrated.
13. A process according to at least one of claims 10-12, characterised by the use of hot hexane as a solvent.
14. A process according to claim 13, characterised by the removal of residual monomers and chloromethane, isopentane or hexane from the solvent tank (26) and/or at least from a following pre-concentration kneader (18.1, 18.3).
15. A process according to at least one of the above mentioned claims, characterised by the production of butyl rubber in a copolymerisation kneader (29).
16. A process according to claim 15, characterised by the use of a pre-concentration kneader (18) for concentration between the copolymerisation kneader (29) and the halogenation kneader (7).

17. A process according to claim 15 or 16, characterised by the occurrence of both copolymerisation (35) and concentration (26) in a combination kneader (34).
18. A process according to at least one of claims 15-17, characterised by the occurrence of copolymerisation and halogenation in a combination kneader (41).
19. A process according to claim 17 or 18, characterised by the separation of the two zones (35, 36, 42) for copolymerisation and concentration or halogenation.
20. A process according to claim 19, characterised by the separation of two zones (35, 36, 42) by influencing the flow of the product.
21. A process according to claim 19 or 20, characterised by the separation of the two zones (35, 36, 42) by mechanical installations in the kneaders.
22. A process according to at least one of the above mentioned claims, characterised by heating of the product before and/or after each kneader.
23. Apparatus for carrying out the process according to at least one of the abovementioned claims, characterised by the use of a halogenation kneader (7) for the production of butyl rubber.
24. Apparatus according to claim 23, characterised in that the halogenation kneader (7) is followed by a final-stage kneader (14).
25. Apparatus according to claim 23 or 24, characterised by at least a pre-concentration kneader (18-18.3) prior to the halogenation kneader (7).
26. Apparatus according to at least one of claims 23 - 25, characterised by the copolymerisation of butyl rubber in a copolymerisation kneader (29).
27. Apparatus according to at least one of the above mentioned claims, characterised by copolymerisation and pre-concentration in a combination kneader (34).

28. Apparatus according to at least one of the above mentioned claims, characterised by copolymerisation and halogenation in a combination kneader (41).

29. Apparatus according to at least one of the above mentioned claims, characterised by the connection between two kneaders with a single or twin-shaft feeding device, where an optional gear pump presses the pasty polymer in an optionally heated connecting tube/connecting heat-exchanger to the following continuous flow device.