

REPLACEMENT OF THE COOLING WITH CaCl_2 MIXTURE WITH THE COOLING USING DIRECT EVAPORATION

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Abstract: *The purpose of the present paper was to find new cooling systems in the rubber manufacturing process.*

Keywords: *synthetic-styrene rubber, autoclaves heat exchange, cooling system, production line, heat exchange coefficients.*

1. Heat Transfer in Autoclaves

1.1. Actual State

At SC CAROM SA, Onesti it is manufactured the CAROM 1500 butadiene-styrene rubber with polymerization in cold emulsion at continuous flow. Generally, through rubber we can understand a compound that has special elastic proprieties at ambient temperature.

Polymerization is the chemical reaction which takes place in autoclaves, where substances with low molecular weight (monomers) are transformed in substances with high molecular weight (polymers).

The reaction system components are: 60% soft or double distilled water, 30% monomers, which constitute the polymerization component, 10% emulsion and initiation agents.

The CAROM 1500 butadiene-styrene rubber has at its core the butadiene (resulted from butane – gas with no color, and pungent smell at 0°C) and α methyl

styrene (resulted from benzene and propylene).

Comparing with the natural rubbers, the butadiene-styrene rubbers have the following positive aspects: better wear strength, better electric isolation properties, better resistance for light action, 20 to 40 times bigger stability for action of Mn, Fe, Cu salts.

The chemical reaction that takes place in autoclaves depends on two basis parameters – temperature and pressure. At a low temperature, the trans 1.4 links content grows and the molecular structure becomes more uniform, figure 1.1. With the temperature decrease, it grows the quantity of polymers chains with stereo regulate structure.

Generally, the temperature has influence on the manufactured rubber quality, as on the optimum polymerization speeds. It has been established that for temperature lower than +5°C, the proprieties of the polymers are no longer affected.

With this considerate, in the autoclaves it is desirable to have temperatures of 6 to 7 °C.

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Also, the pressure is directly influencing the reaction speed – at a high pressure we will have a high reaction speed. This is explained with the fact that once the pressure increases, the macro radicals and monomer molecules collisions frequency is increasing. Practically, the latex pressure in autoclaves is maintained at 5 to 6 bar (with parameters $p=5-6$ bar and $t=5-8$ °C, the butadiene is liquid).

The necessary pressure is given by the latex supplying pump, installed in front of the battery.

The 6-7 °C temperature is supplied through a CaCl_2 mixture cooling, which has a -10 to -4 °C temperature when it moves through the inner serpentine and through the outer layer of the autoclaves.

Each autoclave has a mixing device made of an agitator with two pairs of arms, operated with a 50 rot/min frequency electric motor.

The reaction time is 12 – 20 hours, in which a conversion of 60-70% is obtained. After 20 hours of operating, the reaction speed decreases very much; for example, to get a 1% growth of the conversion it is necessary to extend the reaction time with an hour. Continuing the conversion over 70% can imply negative effects.

The reaction process must be safe from ammonia (which can result in polymerization speed decrease) and copper salt (which restrains the reaction). The admitted limits are: for ammonia <0.02% and for copper <0.0003%.

The technological main phases (preparing the hydrocarbons phase, preparing the watery phase, preparing the mixtures of initiator, activator, catenae regulator, stabilization, the emulsion of the hydrocarbons mixtures with the watery phase, copolymerization and latex gas freeing) take place in E_1 section, where there are installed 6 lines (batteries), each line (battery) having 12 autoclaves, figure 1.2.

The main phase of the process (the copolymerization phase) takes place in one battery, where the preliminary prepared mixture (latex) goes through the 12 battery autoclaves in 10-20 hours. Usually, only 11 autoclaves are used, one remains as a backup.

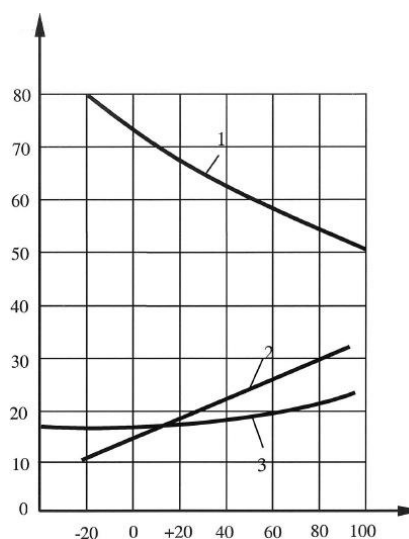


Fig. 1.1. The structure of butadiene-styrene rubber function of polymerization temperature

1. trans 1,4; 2. Cis 1,4; 3. Vinil 1,2

The latex provided by a pump goes through the 11 autoclaves of one battery. At the exit from the last autoclave, a 60-70% conversion must be achieved. There are some methods to limit the conversion rate, like: growth of the supply flow of the battery, or removing one autoclave from the circuit, or lowering the temperature.

Latex production of one production line (battery – made of 12 autoclaves) is $G_L=2.000$ kg/h.

The thermal effect of the copolymerization reaction is $q_R=320$ kcal/kg of formed polymer.

1.2. Cooling Using CaCl₂ Mixture Compared to Direct Evaporation

uniform cooling of the latex mass from autoclaves.

One of the negative aspects of the cooling with CaCl₂ mixture is the not

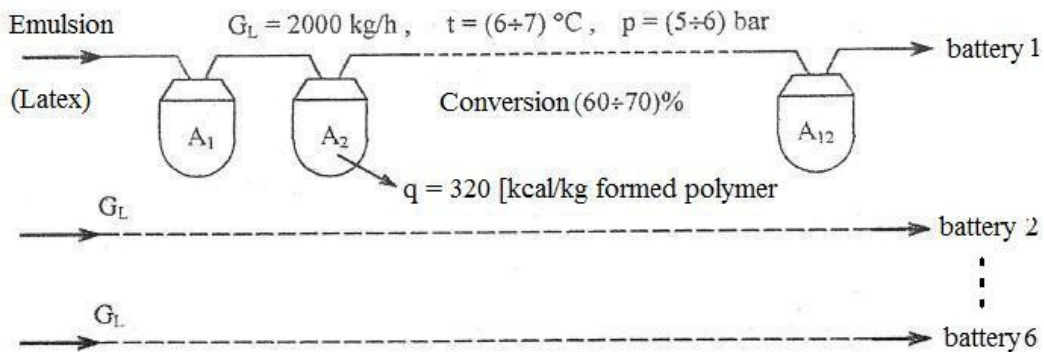


Fig. 1.2. Existing autoclave batteries in section E1
 A₁, A₂, ... A₁₂ – the autoclaves that constitute a manufacturing battery
 G_L – battery capacity per hour [kg/h]
 q_R – reaction heat [kcal/kg of formed polymer]
 t [°C], p [bar] – temperature and pressure of latex that flows through autoclaves

The CaCl₂ mixture enters the autoclaves serpentine with the temperature t , and exits with $t' = t + \Delta t$. The Δt temperature variation in the flux of the cooling fluid produces a temperature variation in the latex mass, which will lower the quality of the manufactured rubber.

The replacement of the CaCl₂ mixture cooling with a process of direct evaporation maintains a constant temperature in the cooling fluid mass $t = t_0$, from entering to exit, this being the evaporation temperature of the used cooling agent. The latex which flows through the autoclave can be maintained easily at a constant temperature (in this case 6-7 °C).

We can add the economic aspect, which is that, through the replacement of the CaCl₂ mixture with a cooling agent, the flow of the fluids is reduced, this way lowering the cost with materials and electric energy.

1.3. Problems that Must Be Considered at Direct Evaporation Cooling

There have been taken into account the following: choose a non polluting agent, the cooling agent must be compatible with the technological process (for example, the ammonia vapors in maximum proportion of 0.02% in the latex mass will have as consequence the accentuate lowering of the polymerization speed, the cooling agent must be easy to obtain, the working parameters of the cooling cycle must be in accessible range, with an easy and precise adjustment possible, there must not be any traces of oil in the cooling agent; the last condition is imposed by two factors: the presence of the oil on the heating exchange surfaces reduces the heat transfer process intensity and the actual construction solution of the cooling serpentine inside the autoclaves does not permit the oil evacuation, which will accumulate in time.

In accordance with the previous statements, it has been chosen for cooling

agent, the propane (C_3H_8), which is in conformity with the first four statements, as regarding the fifth, the cooling agent, the propane, will have to be aspired and compressed by a piston compressor without oiling. This way, the cooling agent will enter the cooling serpentine of the autoclaves without any traces of oil.

2. The Cooling Unit

2.1. Choosing the Cooling Type

In accordance with the data presented in sections 1.2 and 1.3, it has been concluded to choose the direct evaporation cooling, with propane as cooling agent.

The cooling unit must have compressors with membrane or piston compressors without oiling.

2.2. The Flow of the Cooled Agent (Latex) and the Cooling Agent

The heat resulted from the reaction in the autoclaves is taken by the cooling agent (propane) during the direct evaporation process.

The latex flows through the interior space of the autoclave, figure 2.1, at a pressure of 5-6 bar and a temperature of 6-7 °C.

The cooling agent flows through the cooling serpentine inside the autoclave, figures 2.1, 2.2, also, through the exterior serpentine from the exterior cooling layer of the autoclave, figure 2.3. The evaporator of the cooling unit is made of these serpentine. The cooling agent enters the serpentine in liquid state, L_{si} , L_{se} and, due to the heat q_R taken from the reaction process in the autoclave, it evaporates, exiting into the vapor state, V_{si} , V_{se} , figures 2.2, 2.3.

2.3. Design Data

Based on the made analyze, the following data resulted:

- cooling capacity:
 $Q_0=1.000$ [kW/battery] or
 $Q_0=860.000$ [kcal/h, battery]
- the cooling agent evaporation temperature: $t_0=-5$ [°C]
 to which it corresponds
- an evaporation pressure: $p_0=4$ [bar]

Using STAS 1907-68 and 6648-70, for the climateric region of Onesti, the following temperatures are corresponding: in the winter -18 °C and in the summer +25 °C.

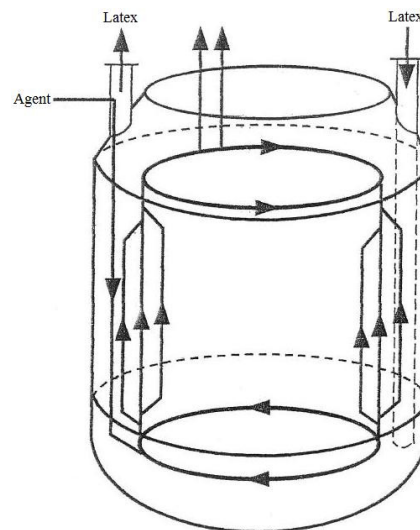


Fig. 2.1. *The flow of latex and cooling agent in the autoclave without exterior cooling space*

In these conditions, for the temperature and the pressure of the cooling agent, the following values are used: $t_c=40$ [°C], for which we have $p_c=13,74$ [bar]. These are the basic parameters for the functioning of the cooling unit.

For a production line (battery), made of 12 autoclaves, the cooling unit must have a cooling capacity $Q_0=1.000$ [kW], in the condition of a evaporation regime at $t_0=-5$ [°C] and $p_0\approx 4$ [bar].

Based on the previous data, the cycle of the cooling unit in the log p - i diagram can be made, shown in figure 2.4. Using the cycle from figure 2.4 and the principle scheme of the unit, figures 2.5, 2.6, the main phases of the cooling process can be distinguished.

The liquid propane enters the in the SAL (Separator Accumulator Liquid) reservoir at parameters $t_0 = -5$ [°C] and $p_0 = 4$ [bar] (phase 4'), from where it is sent by the pump P in the evaporators V. Here, taking the evaporation heat Q_0 from the latex mass, it will evaporate, and will be aspirated by the compressor C (phase 1). The aspirated vapors (phase 1) get, after the compression, in phase 2, at pressure $p_c \approx 14$ [bar] and temperature $t_2 \approx 50$ [°C].

Next, the vapors are cooling and are condensing in the condenser C_d at pressure $p_c \approx 14$ [bar] and temperature $t_2 \approx 40$ [°C], after which, through the lamination in the lamination valve VL, the phase 4' is again achieved, at parameters t_0 and p_0 .

Depending on the construction firm, the cooling unit, besides the mentioned basic elements in figure 2.5, can have a sub cooler with water (SRA), a sub cooler with cooled vapors (SRVR), etc., using an improved cycle, figure 2.4.

Some basic parameters are determined: $q_0 = i_1 - i_4$ [kcal/kg], the specific cooling capacity of the unit, which, as we can see, is given by the enthalpy differences corresponding to phases 1 and 4', figure 2.4.

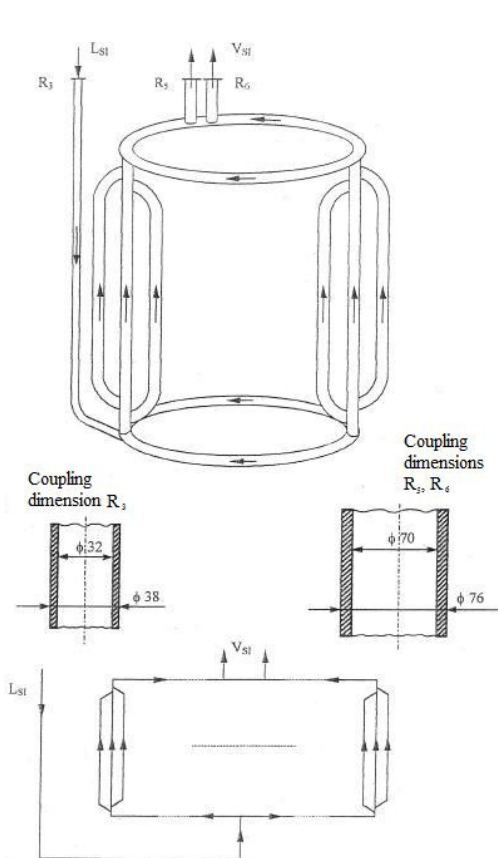


Fig. 2.2. The scheme of the cooling agent flow in the interior serpentine

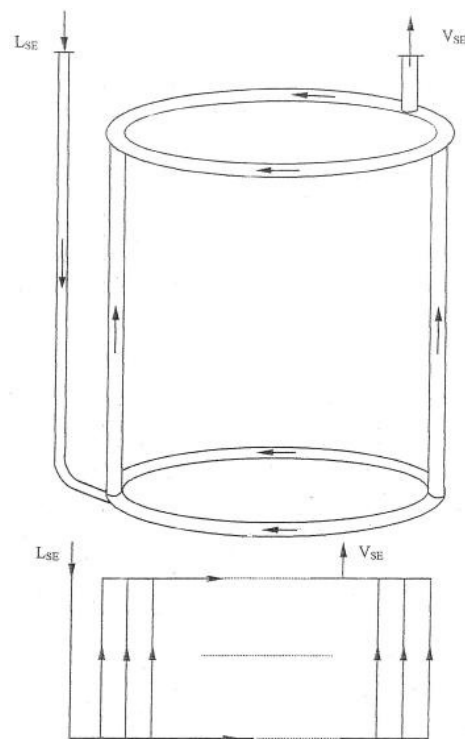


Fig. 2.3. The scheme of the cooling agent flow in the exterior serpentine

We will obtain:

$$q_0 = 189,19 - 100 \approx 90 \text{ [kcal/kg].}$$

Other basic parameters:

$$G=Q_0/q_0=860.000/90 \text{ [kg/h, battery]}$$

$$G=9555 \text{ [kg/h, battery]},$$

the mass flow of propane, which supplies the evaporators.

Knowing the specific volume v' of the liquid, we can write:

$$D=G \cdot v'=9555 \cdot 0,00186 \text{ [m}^3\text{/h, battery]},$$

$$D=17,77 \text{ [m}^3\text{/h, battery]},$$

which represents the volume flow of liquid propane.

Also, knowing the specific volume of the vapors v'' , we have:

$$V=G \cdot v''=9555 \cdot 0,113 \text{ [m}^3\text{/h, battery]}$$

$V=1083 \text{ [m}^3\text{/h, battery]}$, which is the vapor flow aspired by compressor – this being a basic characteristic for design, also in choosing of a compressor.

We have $P_c \approx 178 \text{ [kW/battery]}$, which is the power needed for the compressor. At the condenser, the amount of heat needed to be evacuated is:

$$Q_c=Q_0+P_c=860.000+152.880$$

$$Q_c=1.012.880 \text{ [kcal/h, battery]}$$

$$\text{or } Q_c=1.000+178=1178 \text{ [kW/battery]}$$

$$L_c=G \cdot l=9555 \cdot 16 \text{ [kcal/h, battery]}$$

$$L_c=152.880 \text{ [kcal/h, battery]},$$

$$l_c=i_2-i_1=205-189,19 \approx 16 \text{ [kcal/kg]},$$

and for all the agent flow:

The cooling unit will have an efficiency

$$\varepsilon=Q_0/P_c=1.000/178=5,6$$

Remark: The values previously obtained are informative; the exact values depend on the compressor type.

2.4. Supplying Schemes

Following, there are presented the supplying schemes with cooling agent of the autoclaves serpentine, figure 2.7, also the whole battery of autoclaves, figure 2.8.

2.4.1 The Cooling Agent Supplying of the Autoclaves Serpentine

The liquid propane, L_A , figures 2.7, 2.8, laminated, coming for the SAL reservoir, enters, a part, L_{se} , in the exterior serpentine of the autoclave, and another part, L_{si} , in the interior serpentine. The vapors formed during boiling go out from the serpentine through V_{se} and respectively, V_{si} , being collected in the collector C, and from here, through V_A , they come back in the SAL reservoir.

2.4.2 The Cooling Agent Supplying

Each battery, 2 and 3 respectively, is supplied separately from a cooling unit, figure 2.8. This way, the battery 2 is supplied with cooling unit 1. The liquid cooling agent, laminate through the valve VL, comes in the SAL reservoir and from here is sent by the pump P, through pipe

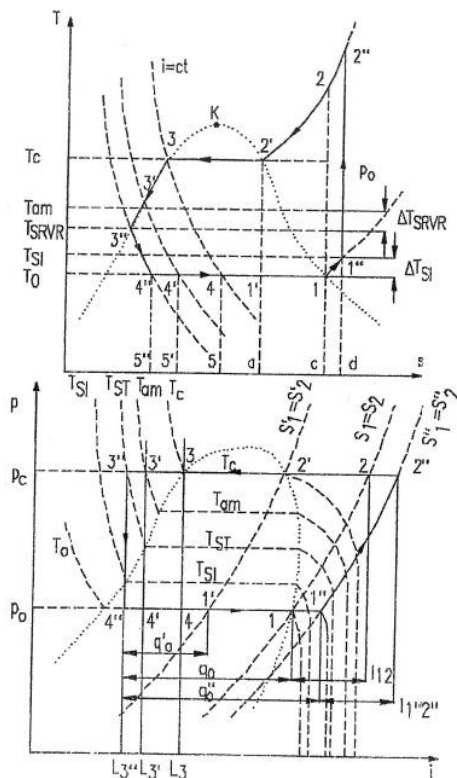


Fig. 2.4. Improved cycle $p-i$ and $T-s$ diagrams

The specific mechanical work done by the compressor is:

L_A , to all the 12 evaporators V (one evaporator V being formed by the interior and exterior serpentine from one autoclave A). The vapors formed in the evaporators are collected in the pipe V_A and returned to the SAL reservoir. From here, the vapors are aspired and compressed in the compressor C, and the resulting liquid is collected in the reservoir R_{ZL} laminated in VL and sent to SAL.

Similarly, the battery 3 is supplied by the cooling unit 2.

Besides the two cooling units 1 and 2, there is needed as backup at least one compressor with cooling capacity $Q_0=1.000$ [kW].

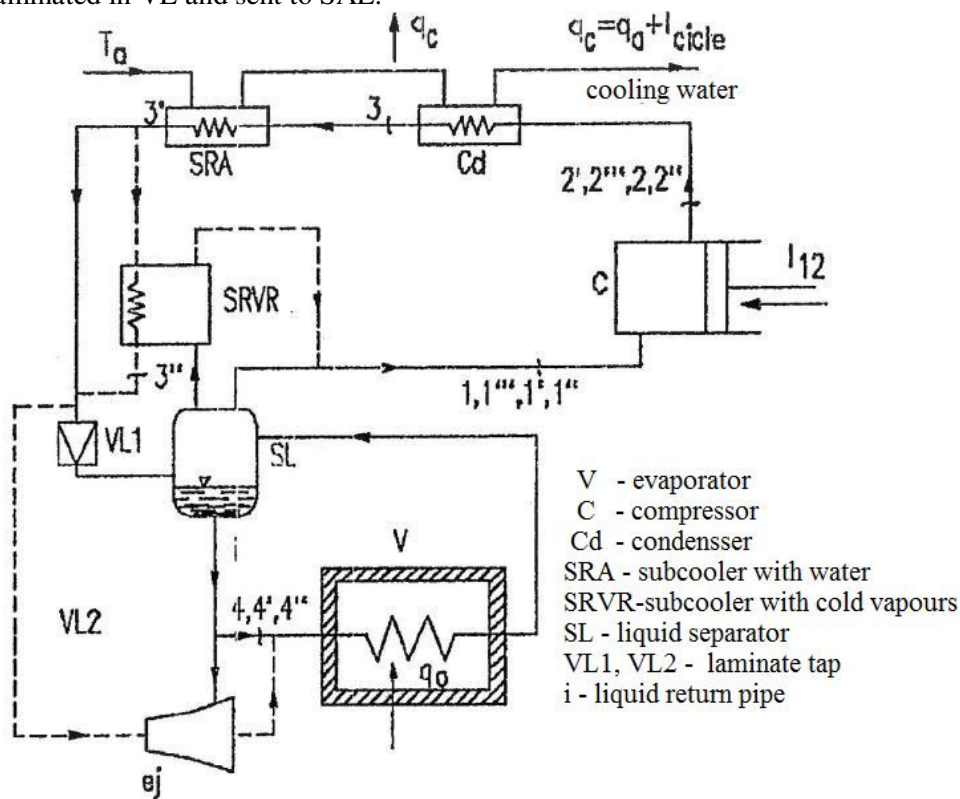


Fig. 2.5 The improved scheme of the vapor agent mechanical compressing unit

2.4.3 Aspects Regarding the Compressors Station

Depending on the work variant adopted, the factory will purchase the needed compressors, which have working parameters in the design data range mentioned in section 2.3.

The basic elements of the compressors station – compressor, condenser, liquid reservoir, sub coolers, adjustment and

automate devices – are to be provided by the factory (together with the compressor units). Usually, the cooling units delivered by the constructor have all the elements stated above.

The cooling of the condenser is usually done with air, water or mixed (air + water) - the variant chosen by the compressors constructor. At former TEHNOFRIG factory, there were manufactured atmospheric condensers with vertical pipes

with 100.000, 200.000 and 400.000 kcal/h, built with panels of 25.000 kcal/h each panel, with the cooling surface of 14 m².

At 100.000 kcal/h it is needed 20 m³/h cooling water.

The heat evacuated at the condenser (section 2.3 - figure 2.4) will have the value around Q_c=1178 kW/battery. The exact value depends on the type of compressor used, working regime and climateric conditions.

2.5. Compressors and Cooling Units Manufacturers

From known data, on a world scale, there are manufactured compressors with membrane at 220 kW and compressors with pistons without oiling at 1300 kW.

Although, their manufacturing is more pretentious compared to the usual compressors (with oiling), in present days, the big manufacturers managed to realize compressors without oiling for a large scale of pressures.

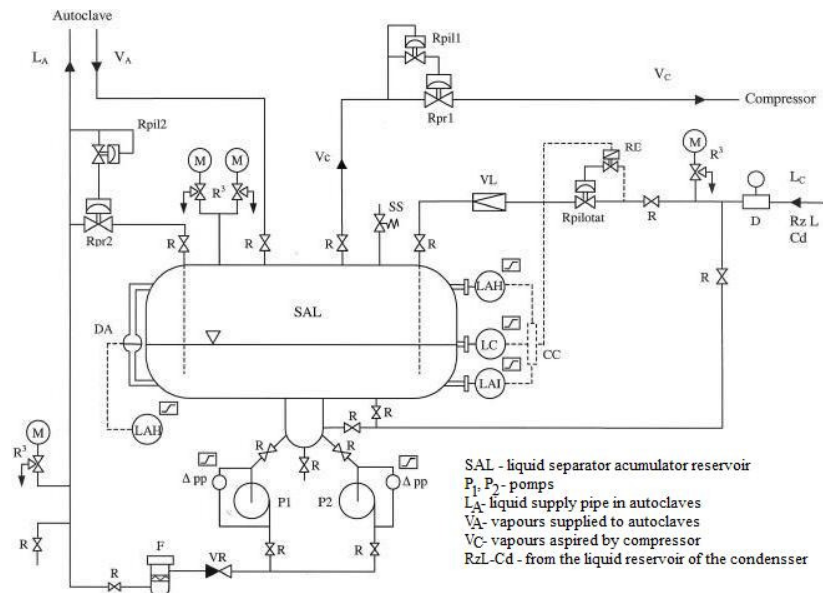


Fig. 2.6 The regulation and automation devices installed on SAL

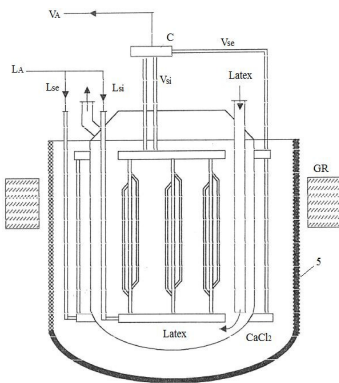


Fig. 2.7. The autoclave with the interior and exterior serpentine

They are used especially in cryogenics, in processes of gas separations, where the cooling agent must not have traces of oil.

Forward, it is presented one of the important compressor manufacturer, which manufactures compressors and cooling units which suits our needs.

In the case of accepting of one working variant from any manufacturer, it is necessary to get in touch with the manufacturer to purchase the corresponding cooling units.

The compressors characteristic needed for the production lines (batteries) 2 and 3 from the station E₁ are presented in section 2.3 – the working parameters for the cooling units.
 Manufacturer contacted:
 BURTON CORBLIN Ltd.

Rue Roland Vachette
 BP 800001
 60181 Nogent sur Oise Cedex
 FRANCE
 Tel +33 (0) 3 44 74 41 00
 Fax +33 (0) 3 44 71 72 43 (Sales)

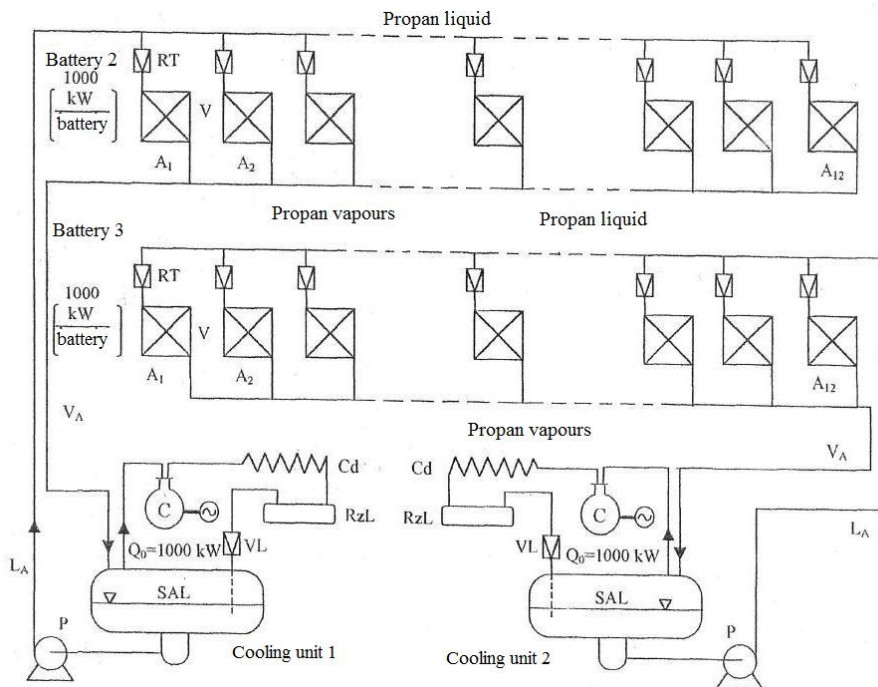


Fig. 2.8 The supplying scheme on the whole battery

Answer: they manufacture compressors with piston (up to 1760 HP), including without oiling, also compressors with membrane (up to 300 HP).

The main characteristics of the compressors are represented in the next table (Table 1) and diagrams (figure 3.1).

Main characteristics of compressors

Table 1

| Nr. crt. | Specification | MU | Compressors with membrane | Compressors with piston | |
|----------|------------------------|-------------------|---------------------------|-------------------------|-------------|
| | | | | Without oiling | With oiling |
| 0 | 1 | 2 | 3 | 4 | 5 |
| 1 | Flow (max) | m ³ /h | < 200 | < 1700 | < 1700 |
| 2 | Exit pressure (max) | bar | < 1000 | < 100 | < 220 |
| 3 | Exit temperature (max) | °C | < 230 | < 220 | < 220 |
| 4 | Power (max) | HP | < 300 | < 1760 | < 1760 |
| 5 | Step compression ratio | - | 20 : 1 | 7 : 1 | 7 : 1 |

3. Conclusions

3.1. The Propane (C_3H_8)

It is a cooling agent with satisfying properties and it is easy to be procured by the factory.

3.2. The Lack of Oiling

It is important that the compression systems (compressor) must not introduce oil in the cooling agent.

With this purpose, there must be used compressors with membrane or compressors with piston without oiling.

Taking into account the high heat quantities that must be evacuated, compressors with piston without oiling must be preferred. The compressors with piston without oiling are highly used in cryogenics, in gas separation processes, where the fluids must not have traces of oil. In section 2.5 there is presented an important manufacturer of compressors and cooling units.

The cooling units must satisfy the conditions stated in section 2.3.

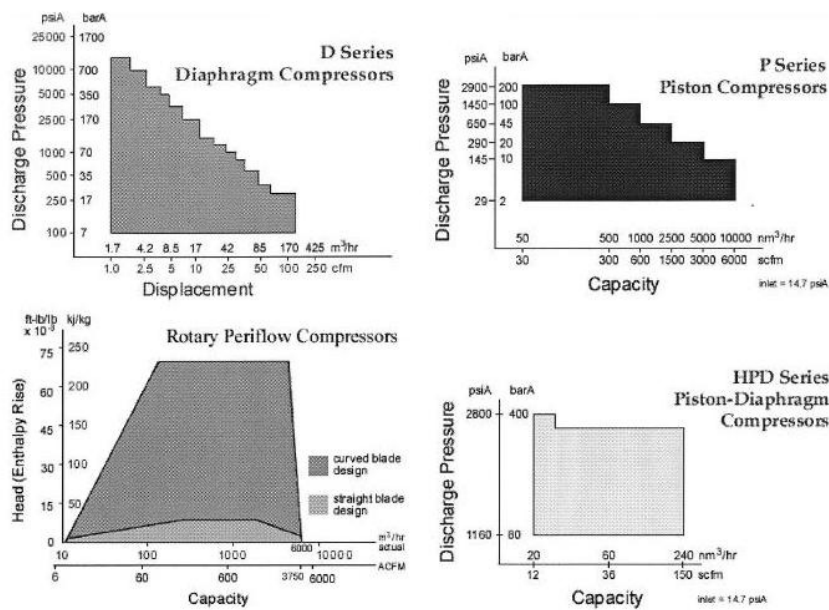


Fig. 3.1. *Compressors diagrams*

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