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THE ROMANIAN CARON RUBBER IN
CONTINUOUS DEVELOPMENT ^{1/}

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THE ROMANIAN CAROM RUBBER - IN CONTINUOUS DEVELOPMENT

10 years ago - in May 1963 - the first bale of Romanian styrene-butadiene synthetic rubber was produced at the Petrochemical Plant of Borzești. The production began with Carom 1500^{x)} followed shortly afterwards by the types 1502 and 1714. The rubber production has grown year by year and the range of assortments was enlarged, the CAROM group being completed by the types 1507, 1508, 1778, CAROM 60 - all of them introduced into the current manufacture, as well as other types: CAROM 1503, 1714, 8401, CAROM N the technology of which has been worked out for laboratory and pilot plants following that in the near future they should be tested in industrial plants too. The production of latexes with special uses is in an advanced stage; some of them have been already obtained in industrial plants: the polybutadiene, polystyrene, butadiene-styrene, butadiene-acrylonitrile latexes a.s.o., whereas others are in the stage of laboratory and pilot plant research.

I. RUBBER

The main physical, chemical and mechanical characteristics of the CAROM rubber are indicated - by type - in Table 1.

x) According to the international classified list for the butadiene-styrene emulsion rubbers.

TABLE 1

THE CAROM RUBBER. PHYSICAL, CHEMICAL, MECHANIC CHARACTERISTICS

Type of rubber	1500	1502	1507	1508	1712	1970
Emulsifier	AR	AG+AR	AG+AR	AG	AG+AR	AG+AR
Stabilizer	S	NS	NS	NS	S	NS
Content of volatile matter at max. 150°C	0,75	0,75	0,75	0,75	0,75	0,75
A s h	0,8	0,8	0,8	0,8	0,8	0,8
Content of iron % max.	0,004	0,004	0,004	0,004	0,004	0,004
Content of stabilizer, %	1...2	1...2	1...2	1...2	1...2	1...2
Content of free organic acids, %	5,00-7,25	4,75-7,00	4,75-7,00	4,75-7,00	3,90-5,70	3,90-5,70
Content of soap max. %	0,5	0,5	0,5	0,5	0,5	0,5
Content of bound styrene monomer	22,5-24,5	22,5-24,5	22,5-24,5	22,5-24,5	22,5-24,5	22,5-24,5
Content of oil gr. per 100 gr. polymer	-	-	-	-	37,5	37,5
Type of oil	-	-	-	-	IA	IA
Mooney viscosity ML (1+4) 100°C	46...58	46...58	30...38	46...58	46...58	46...58
Traction resistance kgf/cm ² min.	260	210	200	240	200	200
						Vulcanization at 50' and 145°C
Elongation at break %min.	550	570	550	550	500	500 do
Modulus kgf/cm ²	56-84	54-79	50-85	56-84	35-65	35-65 do

AA - resin acids soap ; AG - fat acids soap ; S - dark colour ;
NS - light colour, IA - highly aromatic ; N - Naphthenic.

FIELDS OF UTILITY :

1500 - General use rubber, mainly used in the manufacture of tyres and technical items.

1502 - Mainly used in footwear, technical items, sanitary items, toys, etc. - light colour.

1507 - Low plasticity rubber, used especially in the footwear production.

1508 - Light coloured rubber used in the production of high impact polystyrene.

1712 - Rubber completed with aromatic oil, used in the manufacture of tires, technical items and footwear.

1778 - Rubber completed with naphthenic oil, mainly used in the production of footwear and technical items.

By own laboratory and pilot plant researches, new technologies have been worked out for the synthesis of some new CAROM types : 1507, 1508, 1778 and the technologies for the initial types of rubber have been improved - 1500, 1502, 1712 : conversion, optimum emulsifiers dosages and ratios, monomers and aqueous stage. Also, starting from the research works recently carried at C.P. Borzetti for using some new and more active initiation systems in the interpolymerisation process, the expansion of the existing capacity of the synthetic plant by about 30% is being planned with no important further investments.

At present, continuous work is carried in the laboratory and pilot plant for drawing up technologies for new types of CAROM rubber - with improved dielectric characteristics (type 1503), completed with much aromatic (type 1714) oil

(50 p.p. oil for 100 p.p. polymer), emulsion rubber used in the production of the high-impact polystyrene ; also much work is carried for the finalization of the technology for obtaining the butadiene-acrylonitrile rubber (CAROM N) with high resistance to oils, gasoline and organic solvents.

Table 2 indicates several main characteristics of CAROM N.

TABLE 2

CAROM N. CHARACTERISTICS

Type of rubber	Content of acrylonitrile %	Polymerization conditions	Stabilizer	Mooney viscosity (ML-112) 100°C	Plasticity Defo (gr.)/elastic recovery (mm)	Mooney Plasticity ML (°C) 125°C
1	2	3	4	5	6	7
CAROM N	32	cold	S	65±5	3000/30	47
PERDUNAN -M 3310	34	warm	S	65±7	2000/28	49
POLYMER BRITIC - 800	34	cold	NS	83	6000/38	75

TABLE 2

(continued)

Preval- tion (+ 5°)	Speed of prevul- canization (+ 30°C)	Shore hardness at 30°	Fracture resistance cc - 30° kgf/cm ²	Modulus 100% kgf/cm ²	Tearing resis- tence kgf/cm ²	Breaking tension %	Variation in gasoline			
							after 24 h	72 h	after 24 h	
6	9	10	11	12	13	14	15	16	17	18
19'50''	4'	81	235	56	158	320	+1,67	+2,6	0,56	0,96
16'	1'47''	75	208	41	148	290	+1,67	+2,6	0,56	0,96
19'10''	3'	75	165	47	52,5	165				

Table 2 indicates some of the main characteristics of this latter type of rubber - CAROM N - raw and vulcanized - synthesized on continuous pilot and semiindustrially manufactured.

One may notice from this table the similarity between the characteristics of CAROM N and the imported standard rubber. The synthesis technology of this type of rubber is based on the interpolymerization in emulsion of butadiene and acrylonitrile (various ratios butadiene/acrylonitrile depending on the type of rubber one wishes to obtain) in the presence of anion emulgators using the Redox system of initiation and the tertial dodecylmercaptan as a chain regulator. The polymer is separated from the latex by coagulation with salt and acid.

II. THE RESIN 'CAROM 60'

The resin 'CAROM 60' is produced by coprecipitation from latex of the butadiene-styrene copolymer with high content of bound styrene and normal CAROM. The synthesis of the copolymers with high content of styrene is achieved in a continuous or discontinuous process using normal initiation systems ($K_2S_2O_8$) or Redox type depending on the temperature system and the conversion where the polymerization reaction takes place. The coprecipitation of the two copolymers is made with electrolytes and acids under special conditions of temperature, pH, concentration and ratio between the reactants.

Table 3 indicates the physical and mechanical characteristics of CAROM 60, very similar to the characteristics of the imported products - Polysar SS 260.

TABLE 3

Symbol	Time of vulcanization minutes	Breaking resistance kgf/cm ²	Breaking tension %	Remain. tension %	Hardness °Sh A	Mooney plasticity 100°C	Mooney prevulcanization minutes
<u>CAROM 60 - LABORATORY</u>							
DNA-95	10	98;103;101;	460; 500; 460	118	92	75	20
	20	101; 96; 93	380; 340	80	95		
<u>INDUSTRIAL</u>							
	8'x9 at	107;113;99	420;420; 420		95		
	steam	105;106;113	380;380; 380		91		
<u>POLYSAR - LABORATORY</u>							
	10	101;101;98	380 ; 380	92	95	72	19
	20	104; 98;99	340 ; 350	80	95		
<u>INDUSTRIAL</u>							
	3'x 9 at	109;108; 111	420		95		
	steam	112; 110 104	420		95		

III. SYNTHETIC LATEXES WITH SPECIAL USES

The production of the synthetic latexes with special uses has preoccupied the researchers of Borzesti from the very start-up of the rubber plant because they had a basic synthesis technology similar to the technology of the butadiene-styrene emulsion rubber

The laboratory had discontinuous and continuous pilot plants of different capacities (30 - 7,000.kg latex/day) and the direct co-operation of the customer researchers.

Thus laboratory and pilot technologies for different latexes have been worked out ; some of them are already produced on an industrial scale and others are being tested by the customers.

- CAROM S-It polystyrene latex - mainly used to impregnate the textile tissues used especially in the footwear factories for heel counter stiffeners and toe caps. The main characteristic of this latex and of the impregnated materials are given in Table 4.

TABLE 4

Characteristics LATEX CAROM S-It	Characteristics of impregnated tissue	Provided condi- tions	Achieved parame- ters
Aspect : aqueous emulsion	Weight of impreg- nated tissue g/m ²	570 ± 40	540
Content of dry matter % min. 40	Temperature of softening in dry medium °C min.	100	100
Molecular weight medium, min. 300,000	Resistance at tem- perature in water of 37°C min hours	24	24

softening point °C min.	80		
pH	8-10	minimum adherency kg/cm ²	1,5 1,5

The synthetic latex CAROM S-It is manufactured at C.P. Borzesti.

- The synthetic butadiene-acrylonitrile latex CAROM BN - T is mainly used to obtain artificial trades and industrial gloves resistant at kerosene products, solvents, oils. This year the latex CAROM N has been produced for the first time at the industrial plant of C.P. Borzesti. This latex has superior gluing characteristics, produces an elastic resistant film with superior stability towards organic solvents.

TABEL 5
LATEX CAROM BS-H

Characteristics LATEX CAROM BS-H		Characteristics of paper treated with latex	Latex Uni- royel	Latex CAROM BS-H
1		2	3	4
Aspect	- aqueous emulsion			
Content of dry matter % min.	- 30	Plucking cm/sec.	103	105
Content of bound styrene %	- 50-60	Covered face pe- netration 1000/mm	14,5	13,4
Free styrene % max.	- 1,5	Uncovered face penetration 1000 mm	30,7	24,8
Defo hardness, g pi	-2000-3500 - 8 - 10	Shine % Sec. polish	17 480	15 420
Median diameter of latex A par- ticles	- 600			

- The butadiene-styrene CAROM BS-H latex - is used in upgrading paper and in producing the asphalt with superior hydroisolating characteristics. The good results obtained in testing the CAROM BS-H latex in industrial plants contributed to approving its use in paper production.

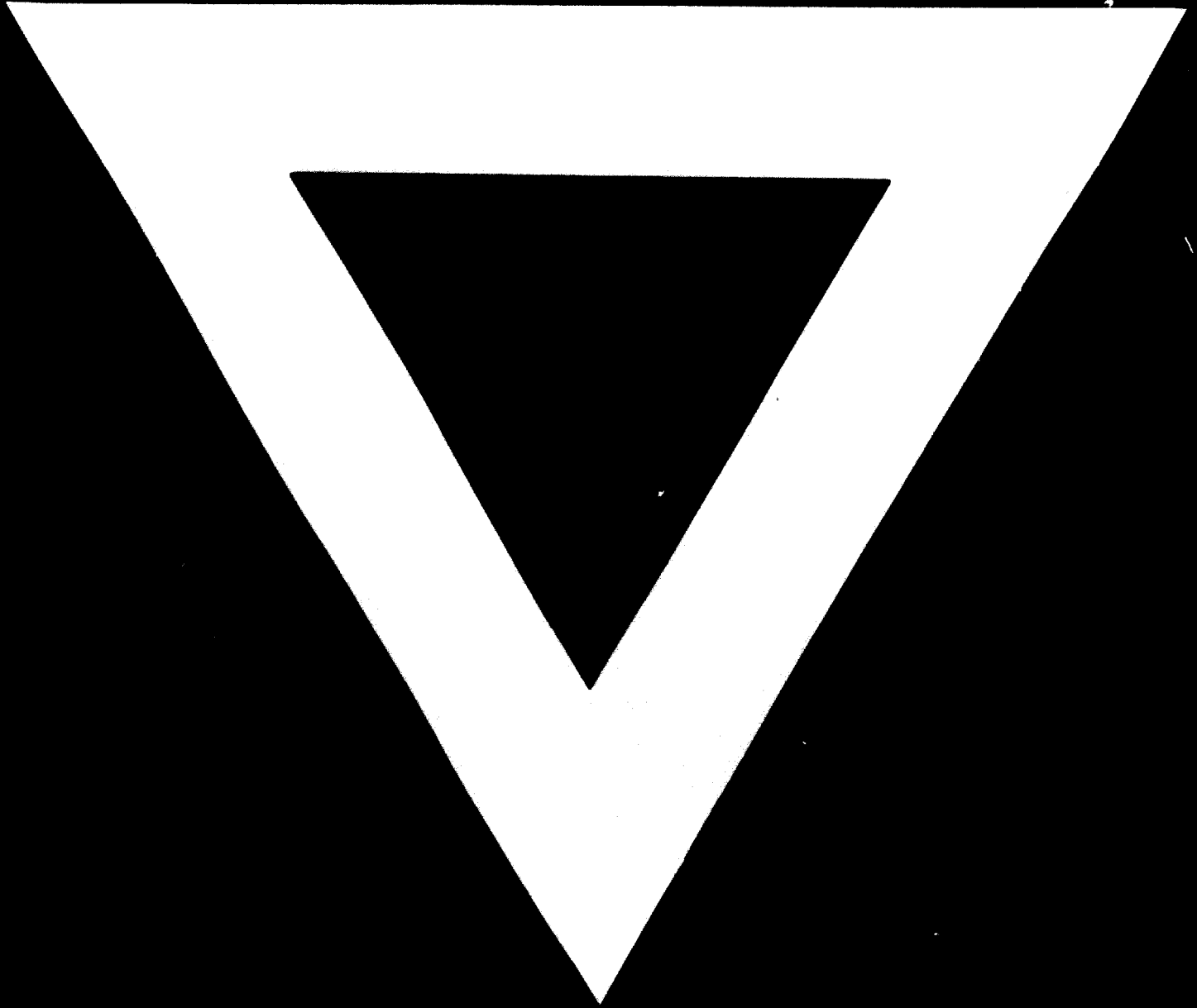
The main characteristics of this type of latex and of the treated paper are indicated in Table 5.

Other types of CAROM latexes are in an advanced stage of research for the manufacture of the tertial ABS copolymer, the impregnation of the cords used in manufacturing tires and conveyer belts, the impregnation of untissueds, latexes for cements and concretes, spongy products, latexes for protecting the earth from erosion and for preserving humidity, glues and paints a.s.o.

S U M M A R Y

This is a brief presentation of the achievements for improving and working out new technologies of rubbers and synthetic latexes with special uses in the Petrochemical Plant of Borzesti in the last 10 years period (1963-1973).





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