

## ***Spray-drying of Natural Rubber Latices***

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*The production of free-flowing natural rubber by the spray-drying technique was investigated. Experiments showed that an initially free-flowing powder could be produced using a combination of large amounts of a surfactant, a film-forming alginate and a silica. The powder was unstable and started agglomerating almost immediately on being formed. Complete agglomeration of the powder occurred usually within 1½h of its production. A more stable powder was produced however when the partitioning agent was chemically attached to the rubber as in the case of MG 49. Electron micrographs showed that the good storage stability of this powder was due to the attached chemical groups in the rubber.*

*Powdered NR produced by spray-drying had high Mooney viscosities and low bulk densities. Efforts to reduce the Mooney viscosity by peptisation resulted in a poorer quality product. The low bulk density of the powder was estimated to increase the costs of freight and handling by about 50% – 70% compared with baled SMR; and consequently was the major obstacle against its successful commercialisation.*

The technique of spray-drying has been employed in the processing of many well-known products such as milk, feedstuff, pharmaceuticals and detergents. The basic operating principle is simple, and entails the atomisation of a liquid into a drying chamber through which is passed a hot stream of air. The fine spray of liquid is instantly vaporised because of the large liquid surface created by atomisation. The dried powder particles fall to the bottom of the chamber and are removed.

The earliest recorded use of spray-drying for NR latex was in the 1920s by a rubber producing factory in Sumatra where the spray-drier was utilised for directly converting latex into dry rubber suitable for compaction into blocks, rather than for producing a free-flowing rubber powder. More recently, there was a great deal of world-wide interest and publicity on the potential usefulness and future importance of rubber powders in industrial manufacturing processes<sup>1-4</sup>.

Interest in the development of a free-flowing NR powder prompted the setting-up of a commercial spray-drying plant by one Malaysian producer in 1975. At about the same time, the RRIM purchased a laboratory-size spray-drier for its own studies, aimed at identifying, understanding and resolving various difficulties in the production of such a rubber<sup>5</sup>. This paper presents some of the findings of the studies.

### **MATERIALS AND METHODS**

#### ***Latexes and Chemicals***

All latexes used were obtained from the RRIM Experiment Station in Sungei Buloh, and were either fresh field latex, ammoniated to various levels or latex concentrate prepared by centrifugation from the above source; or commercial grade latexes bought from Malaysian latex concentrate producers. All chemicals investigated were laboratory grade reagents

obtained from various well-known overseas chemical suppliers.

### *Spray-drier*

The spray-drier used in the experiments was a gravity-feed 'Anhydro' laboratory, Size 1 model, with both nozzle and centrifugal modes of atomisation available (Figure 1). The typical inlet air drying

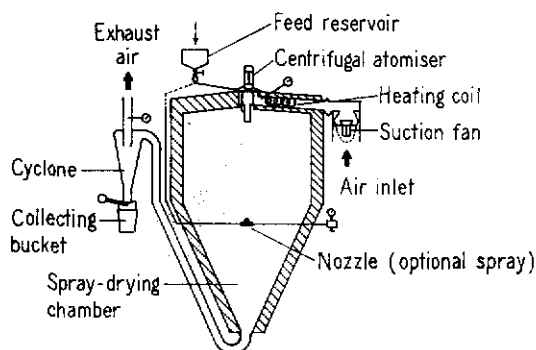


Figure 1. Anhydro laboratory spray-drier.

temperature ranged between 190°C and 200°C while the typical outlet air drying temperature was kept at 95°C ± 5°C.

### *Particle Size Determination*

Particle size and particle size distribution of the powders were determined using a set of sieves on a 'Endecott' mechanical test sieve shaker adopting the test method in ASTM D-1921. The sizes of the sieves used, which were all 'full-height' (i.e. 50 mm high) were 4 mm, 2 mm, 1 mm, 500 $\mu$ , 250 $\mu$  and 125 $\mu$ . Sieving time was 10 min and the sample weight used was 100 grammes. A cumulative distribution curve was plotted, from which the median particle size was calculated. Agglomeration was assessed as the percentage of particles exceeding 2 mm in diameter.

### *Optical (light) Microscopy*

Samples obtained in powder form were sprinkled onto a glass slide and examined dry under the optical microscope using transmitted light at 50X and 100X magnification. A small quantity of the same powder was dispersed in water (approximately 1 g in 5 ml of distilled water), a drop of which was placed on a glass slide, covered with a slip and also examined under the optical microscope at 50X and 100X magnification.

### *Electron Microscopy*

A drop of the suspension (or dispersion) prepared previously for light microscopy was put on a collodion-coated grid, and used for whole-mount examination under the electron microscope. Whole-mount technique was used for dry sample where possible. Where additional information was required, the sample was sectioned. The fixed sample was embedded in a copolymer of styrene and methyl methacrylate after dehydration, and sectioned without staining before examination. The approximate magnifications used were 4000X, 20 000X, 27 000X and 52 000X.

### *Chemical Analysis*

Unless otherwise stated, all chemical analyses were performed using standard RRIM, BS or ASTM methods.

## THEORETICAL CONSIDERATIONS

### *Particle Surface Calculations*

To obtain a free-flowing powder, it is necessary to ensure that the individual rubber particles are effectively covered by the smaller particles of the partitioning agent. The minimum weight of partitioning agent required for effective coverage depends on the relative sizes of the rubber (primary) particles and the partitioning

agent (adsorbed) particles, as well as their respective densities. Assuming that the particles are spherical, and that adsorption is confined to a monolayer, a theoretical expression giving the weight ratio,  $\theta$ , of partitioning agent ( $B$ ) to rubber ( $A$ ), can be derived as:

$$\theta = 3.6276 \left( \frac{\rho_B}{\rho_A} \right) \left( \frac{d}{D} \right) \text{ (Appendix 1)}$$

where  $\rho_A$  = density of the rubber particle

$\rho_B$  = density of the partitioning agent

$D$  = diameter of the rubber particle

$d$  = diameter of the partitioning agent

From the above, it is obvious that to keep the weight ratio low, the partitioning agent used must be of low density and/or have a very fine particle size, particularly if the size of the rubber particle is also small. In practice, the particles are unlikely to be completely spherical, and the adsorption of particles is unlikely to be confined to only one surface layer. Hence, actual weight ratios are likely to be higher than those calculated.

## RESULTS AND DISCUSSION

### *Partitioning Agents for Natural Rubber*

A major limitation of the laboratory spray-drier is that there is no facility for introducing a second spray, simultaneously with the main spray, a feature commonly found in large commercial spray-driers. This means that the partitioning agents have to be added together with the latex in one spray. Since certain chemicals are not compatible with NR latex, this

therefore limited the scope of screening of potentially suitable partitioning agents. Several classes of chemical partitioning agents were investigated.

**Surfactants.** Anionic, cationic, non-ionic and amphoteric surfactants were tested (Table 1). None of the surfactants screened could adequately give a free-flowing NR powder, even at very large loadings of the surfactant (up to 30 p.h.r.), which according to weight ratio calculations should have been sufficient. The more promising surfactants were sodium dodecyl sulphate (SDS) and two non-ionic polyethylene oxide condensates, viz. Teric N 100 (a nonyl phenol ethoxylate) and Teric 200 (I.C.I. Australia). The products obtained using 30 p.h.r. of these three surfactants were fine, fluffy-like materials and not hard agglomerated lumps like those obtained with the other surfactants. The use of two or more surfactants simultaneously did not exhibit synergistic effects and in fact gave less satisfactory results than those using single surfactants.

**Film-forming/encapsulating agents.** One of the techniques used to produce free-flowing materials is to encapsulate the material with a film-forming chemical. For NR, the encapsulating chemical should preferably be polymeric in nature to form a tough, continuous, flexible protective film around each particle. This film should also be non-tacky at ambient temperatures so that it provides the necessary free-flow characteristics; at the same time, it should either melt or decompose at higher temperatures, so as to free the rubber particles and enable their cohesion during the subsequent mixing and moulding operations. The desired melting or decomposition temperature of the encapsulating chemical should be above 100°C, the highest temperature of the spray-dried product, so that the free-flow charac-

TABLE 1. SURFACTANTS EVALUATED AS PARTITIONING AGENTS FOR NATURAL RUBBER

Anionic	Cationic	Non-ionic	Amphoteric
Potassium ricinoleate	Vulcastab TM (I.C.I., UK)	Vulcastab LW (I.C.I., UK)	Amphionic-D (A.B.M. Chemicals)
Potassium oleate		Teric N 100 <sup>a</sup> (I.C.I., Australia)	
Potassium palmitate		Teric N 40 (I.C.I., Australia)	
Ammonium caseinate		Teric N 30 (I.C.I., Australia)	
Sodium dodecyl sulphate <sup>a</sup>		Teric 17A 25 (I.C.I., Australia)	
Teepol (Shell Chemicals)		Teric 16A 29 (I.C.I., Australia)	
Vulcastab LS (I.C.I., UK)		Teric PE 68 (I.C.I., Australia)	
		Teric SF 15 (I.C.I., Australia)	
		Terric 200 <sup>a</sup> (I.C.I., Australia)	

Latex used : HA concentrate

<sup>a</sup>Promising surfactants

teristics of the product are not destroyed by the spray-drying.

Polyethylene and polypropylene are materials which appear to have the requirements of an encapsulating agent for NR. However, aqueous dispersions of these polymers are not available, and therefore could not be tested. Instead, certain film-forming types of alginates were tested. Collatex A/RE Extra, Manutex RK Extra and Manutex RF Extra (Alginate Industries, U.K.) are three commercial alginates with exceptionally good film-forming properties. The low viscosity grades *viz.* Manutex RF/Extra and Collatex A/RE Extra gave higher product yields than the high viscosity grade, Manutex RK/Extra (Table 2). Levels higher than 10 p.h.r. are not reported because the higher viscosity of the resulting latices led to difficulties in spray-drying. It was interesting to note that Collatex A/RE Extra (an ammonium alginate) imparted a darker colour to the resultant rubber compared with the other sodium alginate grades. None of the three alginates gave a

free-flowing product with high ammonia (HA) latex concentrate.

*Inorganic colloids.* Bentonite clay and silica are available in colloidal forms. Consequently, their dispersions were thought to be fine enough and suitable for use in the laboratory spray-drier. Bentonite however, was not easy to use with NR latex. A dispersion of the clay could not readily pass through a paper filter thus suggesting that the particles were not sufficiently fine. As a result, there were clogging problems during the atomisation process. It was also not effective, judging by the non-free-flowing, lumpy rubber obtained, even at 20 p.h.r. of clay. Presumably, due to its high density, the amount of Bentonite used may not have been sufficient to cover adequately the surface of the rubber particles.

Colloidal silica were found to be more promising. It was necessary to develop a technique of generating the colloidal silica *in-situ* in the latex. The technique involves

TABLE 2. ALGINATES EVALUATED AS PARTITIONING AGENTS

Alginate	Amount (p.h.r.)	Bucket yield	Product description
Manutex RF/Extra	5	38	Agglomerated lump
Collatex A/RE Extra	5	32	Agglomerated lump (discoloured)
Manutex RK/Extra	5	20	Agglomerated lump
Manutex RF/Extra	10	44	Agglomerated lump
Collatex A/RE Extra	10	38	Agglomerated lump (discoloured)
Manutex RK/Extra	10	29	Agglomerated lump

Base latex : HA concentrate + 5 p.h.r. Teric N 100

Manutex RF/Extra — sodium alginate, low viscosity grade

Manutex RK/Exrta — sodium alginate, high viscosity grade

Collatex A/RE Extra — ammonium alginate, low viscosity grade

the addition of sodium silicate to the latex, followed by the careful addition of a mineral acid (e.g. sulphuric acid) to pH 9.8 to hydrolyse the sodium silicate and thereby releasing silica in its colloidal form. A small quantity of a non-ionic stabiliser was initially added to the latex to protect it from the destabilising action of the acid. Either Teric N 100 or Teric 200 was used for this purpose. Results show that using about 15 p.h.r. of colloidal silica (as sodium silicate), free-flowing granules of around 5mm diameter were obtained initially, but these gradually agglomerated within  $\frac{1}{2}$  h of spray-drying (Table 3).

Since sodium silicate gives a highly alkaline latex, the use of a low or non-ammoniated latex would reduce the amount of acid required to hydrolyse the sodium silicate. Results show that in addition to this benefit, a non-ammoniated field latex also gave higher product yields and better looking and more free-flowing products than those obtained when starting with the other ammoniated latices (Table 4). Wong and Lau<sup>6</sup> have shown

that ammonia increases the tack of NR by inducing certain changes in the non-rubbers of the latex. This could explain the better free-flowability of the product when non-ammoniated latices are used. A second conjecture is that the lower amount of sulphuric acid required to reduce the pH of the non-ammoniated latex could have improved the free-flowability; since it is known that sulphuric acid coagulated rubbers tend to be more tacky than formic acid coagulated rubbers because of their proneness to oxidative ageing.

*Crumbling agents.* Chemicals which are not compatible with rubber like castor oil and polypropylene glycol (PPG 2000) were tested as partitioning agents. Since they were not miscible with latex, they had first to be emulsified with a small quantity of soap (either potassium stearate or potassium oleate). Results obtained were disappointing. Even at very large levels of these chemicals (20 p.h.r.), the products obtained were not free-flowing, in spite of being oily.

TABLE 3. EFFECTS OF COLLOIDAL SILICA AS PARTITIONING AGENT

SiO <sub>2</sub> (p.h.r.)	Bucket yield (%)	Product description (initial)
5	25	Agglomerated lump
10	48	Lumpy, large and small granules
15	56	Free-flowing rubbery granules

Base latex: HA concentrate + 5 p.h.r. Teric 200 + SiO<sub>2</sub> (as sodium silicate) + dilute H<sub>2</sub>SO<sub>4</sub> to pH 9.8 ----->  
spray-dry

All products agglomerated into one lump after ½ h of production.

TABLE 4. EFFECTS OF AMMONIATION AND LATEX TYPE ON PRODUCT

Latex	NH <sub>3</sub> (%)	Bucket yield (%)	Product description (initial)
Concentrate	0.7	56	Loose rubbery granules
Concentrate	0.2	62	Loose rubbery granules
Field	0.2	61	Loose rubbery granules
Field	0	72	Free-flowing granules

Base: Latex + 5 p.h.r. Teric 200 + 15 p.h.r. SiO<sub>2</sub> (as sodium silicate + dilute H<sub>2</sub>SO<sub>4</sub> to pH 9.8 ----->  
spray-dry

All products agglomerated eventually into one lump, approximately within ½ h of production

*Combinations of surfactants, alginates and silica.* Combinations of a surfactant, an alginate and silica as partitioning agents were also investigated. The main results are summarised in Table 5. Decreasing the level of surfactant used generally gave more problems in spray-drying, probably due to the decreased stability of the latex. The minimum level of Teric 200 required for satisfactory spray-drying was 5 parts per hundred parts rubber. Increasing this level further to 10 p.h.r. gave higher yields and better free-flowing products. The levels of alginate and silica used were less critical to the success of spray-drying; though in general, the higher the levels used the better the quality and yield of the products.

Combinations containing a total of 25 p.h.r. or more of the various additives

successfully gave fine free-flowing powders which agglomerated a short while after production. The resulting agglomerates however remained soft and friable, and were readily broken up by hand provided they were not physically compressed. They could also be readily reverted to a fine free-flowing powder by passing through a high-speed cutter such as a Waring blender; but would re-agglomerate on standing. When the powders were compressed with some force, however, they became hard and non-friable.

#### *Chemical Modification of Natural Rubber as a Means of Partitioning*

It is known that NR latex can be modified by the introduction of certain chemical groups on to the NR chains. Since such chemical groups are per-

TABLE 5. COMBINATIONS OF CHEMICALS AS PARTITIONING AGENTS

Teric 200 (p.h.r.)	Manutex EF/Extra (p.h.r.)	SiO <sub>2</sub> <sup>a</sup> (p.h.r.)	Bucket yield (%)	Product description	
				Initial	Final <sup>b</sup>
5	10	—	44	Agglomerated lump	Hard lump
5	—	15	56	Loose granules	Hard lump
3	10	5	28	Agglomerated lump	Hard lump
1	10	10	26	Agglomerated lump	Hard lump
5	5	5	40	Loose particles	Hard lump
5	5	10	48	Fine granules	Friable agglomerates
5	10	5	47	Loose particles	Hard lump
5	10	10	51	Fine granules	Friable agglomerates
10	10	5	57	Fine granules	Friable agglomerates
10	5	10	52	Fine powder	Friable agglomerates
10	10	10	56	Fine powder	Friable agglomerates

Base latex: HA concentrate

<sup>a</sup>SiO<sub>2</sub> added as sodium silicate and released by acidic hydrolysis.

<sup>b</sup>Refers to 1½ h after production.

manently bound to the rubber, it was thought that they could be more effective partitioning agents than chemicals which are only physically added. Experiments were therefore conducted using various chemically-modified latices to test this hypothesis.

Methyl methacrylate-grafted (MG) natural rubber latices were initially investigated. Untreated MG 49 latex, on spray-drying, gave a product which was initially very powdery but gradually balled up into the form of loose particles, 88% of which was less than 125µ in diameter. The particles were quite free-flowing and not agglomerated even under compaction, quite unlike any of the products obtained previously using unmodified NR latex. On prolonged standing, they tended to cake, but were easily broken up by hand.

Addition of small amounts of sodium dodecyl sulphate (SDS) to the latex

before spray-drying, improved the fineness and free-flowability of the resultant power (Table 6). The tendency to cake on standing was also reduced, probably because of the lower moisture content of the powder. Other surfactants which were just as effective as SDS for improving the powder were Teepol (a sulphated olefin), potassium oleate, Lissapol LS (Sodium oleyl-p-anisidine sulphonate), Teric N 100 and Teric 200 (Table 7). Only 1 p.h.r. of any of these surfactants was sufficient to give a fine, free-flowing powder with MG 49 latex.

When the methyl methacrylate content was reduced as in the case of MG 30 latex, a higher amount of surfactant was required to give a free-flowing powder. Thus, to obtain a powder comparable to that obtained with MG 49, 10 p.h.r. of SDS was needed (Table 8). This strongly suggests that the chemically-grafted methyl methacrylate groups do act as

TABLE 6. SPRAY-DRYING OF MG 49 LATEX

Latex treatment (p.h.r. SDS)	Moisture (%)	Product <125 $\mu$ (%)	Description
0 (Control)	3.0	> 88	Loose particles
0.25	2.0	> 94	Powdery
0.5	1.2	> 96	Powdery
0.75	0.8	> 99	Fine, free-flowing powder
1.0	1.2	> 99	Fine, free-flowing powder
2.0	1.9	> 99	Fine, free-flowing powder

TABLE 7. SPRAY-DRYING OF MG 49 LATEX WITH VARIOUS SURFACTANTS

Treatment (1 p.h.r.)	Product < 125 $\mu$ (%)	Description
SDS	> 99	Fine, free-flowing powder
Teepol	> 97	Loose particles, powdery
Potassium oleate	> 98	Loose particles, powdery
Lissapol LS	> 97	Loose particles, powdery
Teric N 100	> 99	Fine, free-flowing powder
Teric 200	> 99	Fine, free-flowing powder

TABLE 8. SPRAY-DRYING OF MG 30 LATEX

Latex treatment (p.h.r. SDS)	Moisture (%)	Product < 125 $\mu$ (%)	Description
0	2.7	—	Agglomerated lump
1	1.3	—	Agglomerated lump
5	1.3	> 35	Loose agglomerates
10	1.2	> 90	Loose particles, powdery

partitioning agents for NR; though, contrary to earlier speculation, they seem to be less effective since 10 p.h.r. of physically added SDS was equivalent to 19 p.h.r. of reacted methyl methacrylate

content. Alternatively, SDS could be a much better partitioning chemical than methyl methacrylate. It would be interesting to know a method of chemically grafting SDS onto NR so that this could be tested.



Since MG latices of lower methyl methacrylate content were not readily available, other types of chemically modified latices with low degrees of modification were studied; one of these was hydrazine formaldehyde resin-reinforced latex or HF latex. With decreasing levels of hydrazine formaldehyde resin in the latex, increasing difficulty was encountered in getting a free-flowing product even though higher amounts of surfactants were added to the latex. Thus 'HF 7' and 'HF 5' latices gave poorer products using 20 p.h.r. SDS than 'HF 10' latex with 10 p.h.r. SDS (Table 9). This result seems to differ somewhat from the results with higher chemically-modified MG 49 and MG 30 latices, and could suggest that surfactants like SDS are effective partitioning agents for NR with a high amount of chemical modification only and not when the rubber is slightly modified.

#### *Properties of Spray-dried Natural Rubber*

**Particle size.** Powdered NR with particle sizes ranging from  $125\mu$  to more than 4 mm diameter could be successfully obtained by spray-drying latex using a combination of surfactant, alginate and silica as the partitioning agent. However, the free-flowing property of this rubber

powder lasted only a short time, as evident by the changes in its particle size distribution when it was freshly produced and  $\frac{1}{2}$  h and 1 h after production (Figure 2). Complete agglomeration of the powder took place within  $1\frac{1}{2}$  h of production. Table 10 shows a typical analysis of the agglomerated NR powder. Its main features are its high ash content, acetone extract and volatile matter. The low rubber hydrocarbon content reflects the high amount of partitioning agents used. The product also has a high Mooney viscosity, low ageing resistance (PRI) and fast-curing characteristics. Figure 3 shows a typical electron micrograph of the agglomerated NR powder. Discrete particles of silica averaging around  $0.02\mu$  can be seen within the rubber.

Optical and electron micrographs of a free-flowing MG 49 powder were also taken and they showed some interesting features. The powder consisted of single particles and loose clusters of particles. The particles were quite spherical in shape, ranging from  $3\mu$  to  $50\mu$  diameter and mostly averaging  $15\mu$  diameter (Figures 4 and 5). The particle surfaces were not smooth and appeared to be covered by smaller sub-particles (Figure 6). Sectional views at high magnification

TABLE 9. SPRAY-DRYING OF HYDRAZINE-FORMALDEHYDE TREATED LATICES

Latex	SDS (p.h.r.)	Bucket yield (%)	Product description
HF 5	10	2 <sup>a</sup>	Agglomerated lump
HF 5	20	20	Non-free flowing rubbery agglomerates
HF 7	10	10	Agglomerated lump
HF 7	20	21	Non-free flowing rubbery agglomerates
HF 10	10	17	Lumpy, large and small granules
HF 10	20	23	Slightly free-flowing rubbery granules

<sup>a</sup> Run stopped half-way due to clogging of atomiser.

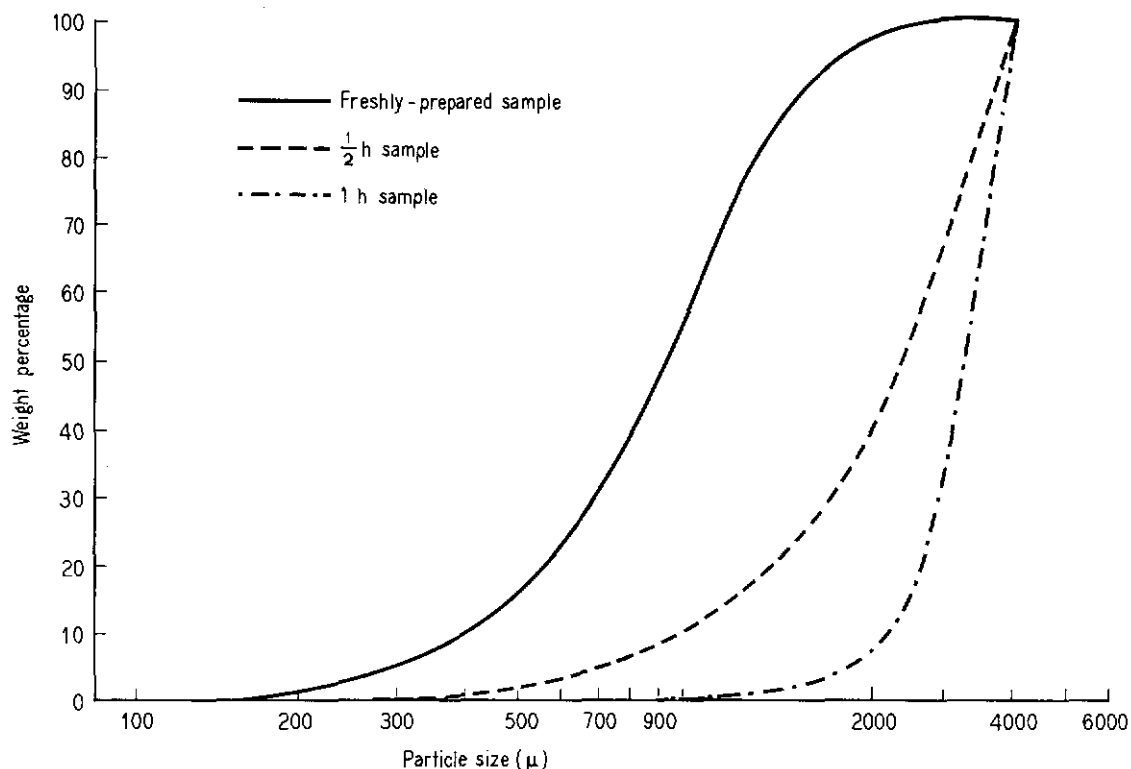


Figure 2. Cumulative particle size distribution curves.

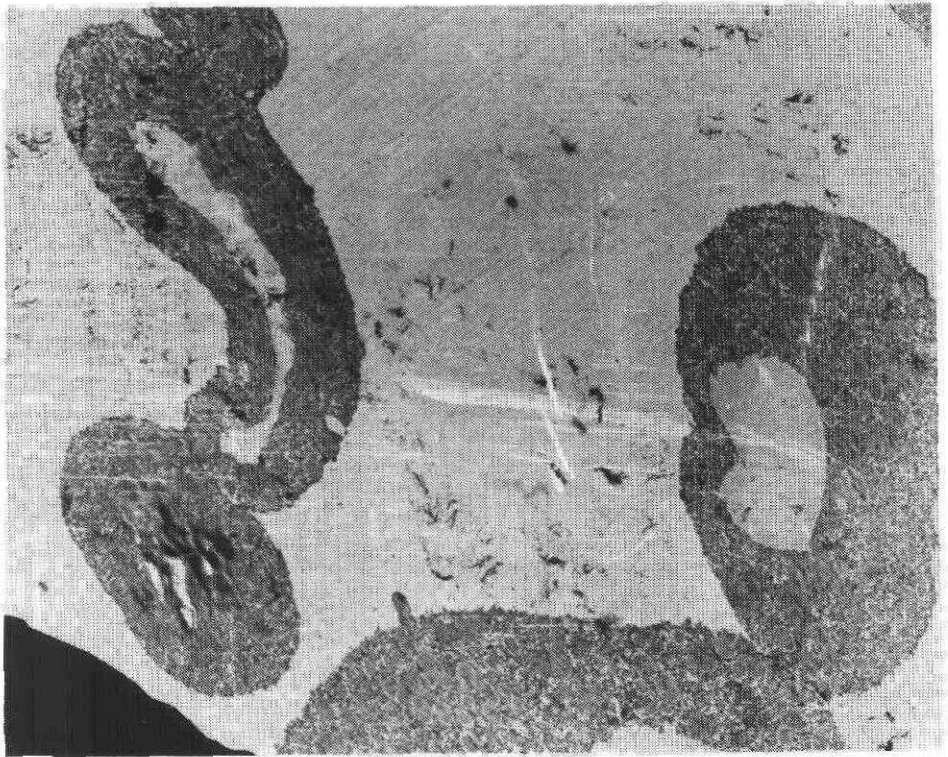
TABLE 10. TYPICAL ANALYSIS OF SPRAY-DRIED NATURAL RUBBER

Property	Typical value
Rubber hydrocarbon (% wt)	76.91
Nitrogen content (% wt)	0.32
Ash content (% wt)	9.45
Volatile matter (% wt)	1.56
Acetone extract (% wt)	13.62
Silicon content (% wt)	3.50
Po	64
PRI	59
V <sub>R</sub> (ML 1 + 4)	112
MOD	8.37

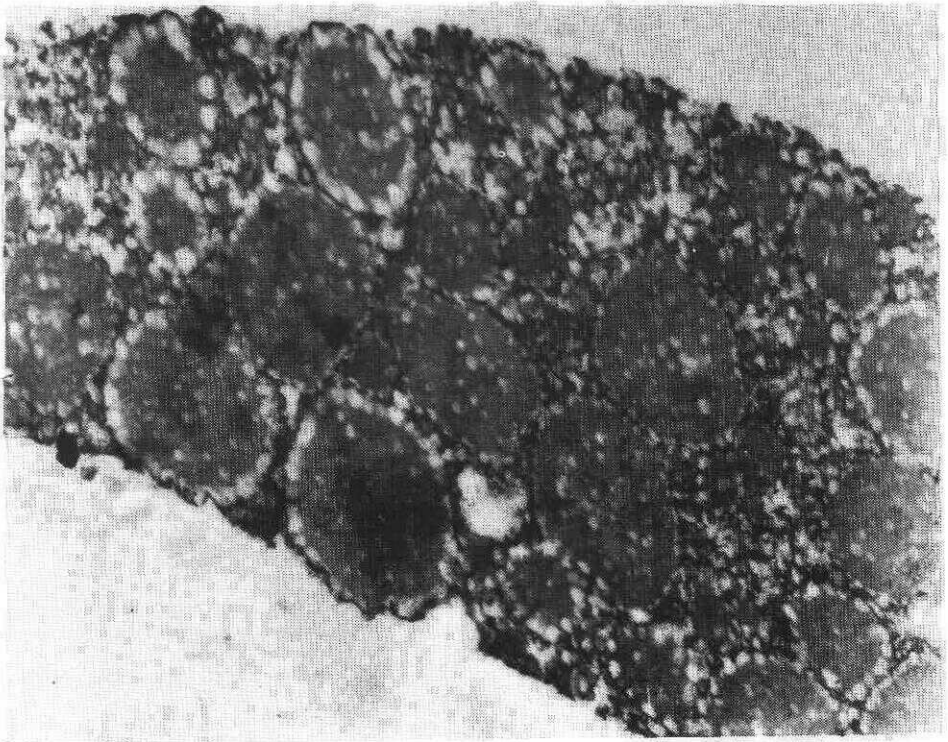
Sample: field latex + 10 p.h.r. Teric 200 + 10 p.h.r. Manutex RF/Extra + 10 p.h.r. silica  
Sample was initially powdery but agglomerated before analyses took place.

(Figures 7 and 8) showed that each large particle contained distinct colloidal latex particles of NR, each of which had been modified by an outer layer of polymethylmethacrylate sub-particles. Thus, the large particles actually represent the 'droplet' particles, the sizes of which are determined by the sizes of the latex droplets formed on spray-drying. This probably explains why they are also cenospheres (hollow spheres), which could result from expanding gaseous forces during the drying process. The rough surface appearance of these particles is probably due to the profiles of the polymethylmethacrylate sub-particles.

**Viscosity.** The most significant effect of spray-drying is the high viscosity of the product. One aspect of this viscosity



*Figure 7. Sectional electron micrograph of MG 49 powder (4158.X).*



*Figure 8. Sectional electron micrograph of MG 49 powder (26 730 X).*

increase is attributed simply to the presence of the inorganic partitioning agent. Thus, the higher the silica content of the rubber, the higher is its Mooney viscosity (Figure 9). The other less obvious viscosity rise is obtained by comparing the extrapolated viscosity of the rubber at zero silica content with the viscosity of an acid-coagulated control derived from the same latex. This increase of about 25 Mooney units can be ascribed to the harsh conditions of the spray-drying, *viz.* the rapid removal of water from the rubber at a temperature of about 200°C, which are equivalent or stronger than those of the accelerated storage-hardening test.

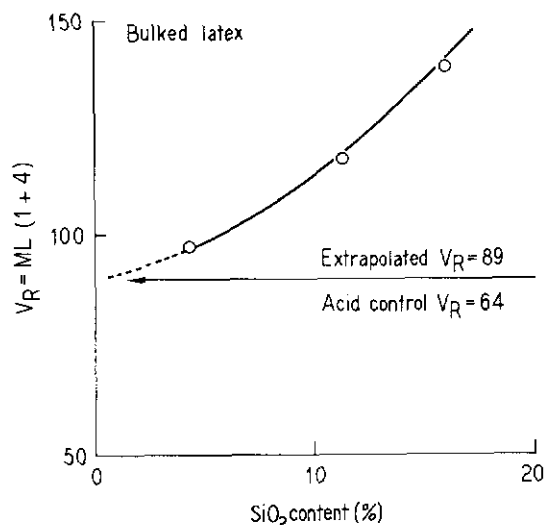


Figure 9. Viscosity on spray-drying versus silica content.

This hypothesis is substantiated by further results with monoclonal latices (Figure 10). A viscosity increase from spray-drying was seen in all three latices. This increase was highest for the softest clone, RRIM 501, and lowest for the hardest clone, PB 86, which therefore

agrees with the above conjecture since a soft clone would have a larger amount of aldehyde groups than a hard clone for cross-linking of the rubber chains and hence viscosity increase.

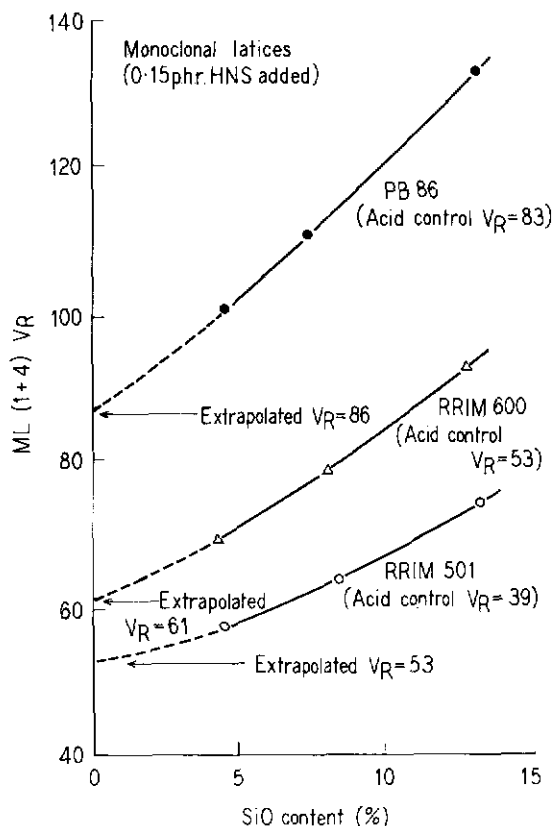


Figure 10. Viscosity on spray-drying versus silica content — clonal differences.

One useful application of powdered rubbers is in solution adhesives. Experiments on the solution properties of spray-dried NR showed a marked influence of the Mooney viscosity of the rubber on its solution (Brookfield) viscosity (Figure 11). For a given solution concentration, the higher the Mooney viscosity of the

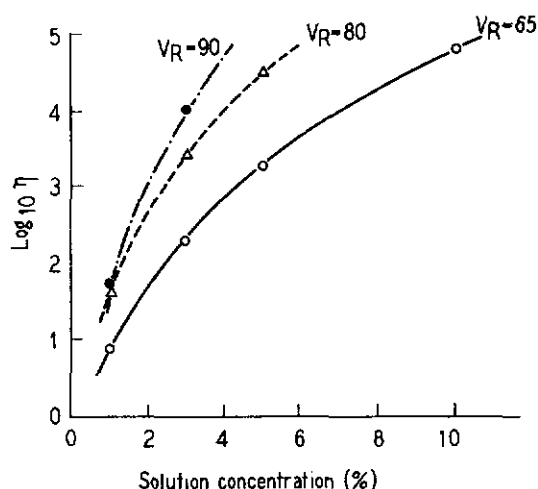


Figure 11. Effects of Mooney viscosity on solution Brookfield viscosity ( $\eta$ ).

rubber, the higher is the solution viscosity. It is imperative therefore to use a low Mooney viscosity rubber as the starting material for preparing powdered NR intended for use in solution adhesives.

Various attempts were made to reduce the Mooney viscosity of spray-dried NR, using peptisers, (e.g. RPA 3 and Renacit VII), oxidising agents, calcium and zinc soap. In all cases where viscosity reduction was achieved, there was always an accompanying reduction in the ageing resistance (PRI) of the rubber, which was at times manifested by the poorer free-flowing characteristics. The addition of antioxidants (e.g. Nonox WSL) did not prevent the lowering in PRI, but did improve the free-flowability of the product slightly. Consequently, a satisfactory method for reducing Mooney viscosity has not been obtained. The only route is to use latices with low rubber viscosities.

**Bulk density.** Powdered NR has a significantly lower bulk density than

baled SMR (Table 11). Powders with small particle sizes like MG 49 have even lower bulk densities due to the increased proportion of voids between the particles.

TABLE 11. BULK DENSITIES OF VARIOUS RUBBERS

Rubber grade/form	Average bulk density (g/cm <sup>3</sup> )
SMR 5 bale	0.898
Powdered MG 49 (free-flowing)	0.528
Powdered NR (free-flowing)	0.608
Powdered NR (agglomerated)	1.015

Powdered NR contains 10 p.h.r. silica (density : 1.95 g/cm<sup>3</sup>)

The economics of handling and freight-ing powdered NR is adversely affected by its low bulk density since freight charges are normally based on the volume of the cargo rather than the weight (Table 12). The freight costs for powdered NR would be about 50% to 70% more than that of baled SMR, depending on the fineness of the powder.

## CONCLUSION

Experiments with spray-drying of NR latices have revealed a number of interesting observations. A free-flowing, spray-dried NR powder cannot be produced without the use of a large amount of partitioning agents. Such partitioning agents may be chemical groups attached to the rubber *via* some chemical reaction (e.g. the polymethylmethacrylate grafts in MG 49 and MG 30), or are discrete chemical entities added to the latex prior to spray-drying (e.g. a surfactant, a film-

TABLE 12. FREIGHT CONSIDERATIONS

Rubber grade/form	Relative freight index
SMR 5 bale	100
Powdered MG 49	170
Powdered NR (free-flowing)	148

$$\text{Freight charges} \propto \frac{\text{Volume of rubber}}{\text{Density}} \quad \text{for a fixed weight}$$

forming agent and an inert, inorganic filler-type material like silica). Chemically attached partitioning agents appear to be more effective in retaining the free-flowing characteristics of the rubber than physically-added partitioning agents, probably because they are permanently linked on to the rubber particle surface. Evidence for this chemical partitioning effect was found in the micrograph studies of MG 49 powder. The large levels of partitioning agents required to give a free-flowing powder are mainly due to the high inherent tack of NR, the smallness of the particles formed by spray-drying and the poor distribution of the partitioning agents within the particle bulk rather than on its surface.

Powdered NR produced by the spray-drying technique have high Mooney viscosities and low bulk densities. Selection of latices with low rubber viscosity is the only present viable means of obtaining a powder with low viscosity; reduction of rubber viscosity by peptisation results in a poor quality product. The low bulk density of the powder affects adversely the economics of packaging, handling and freighting; these costs are about 50% – 70% more than that of baled SMR. This drawback could be the biggest obstacle

against the successful commercialisation of NR in powder form. The high cost of partitioning chemicals, the high energy requirements of spray-drying and the need to use premium latex as a starting material are also factors which will significantly increase the cost of the product.

#### ACKNOWLEDGEMENT

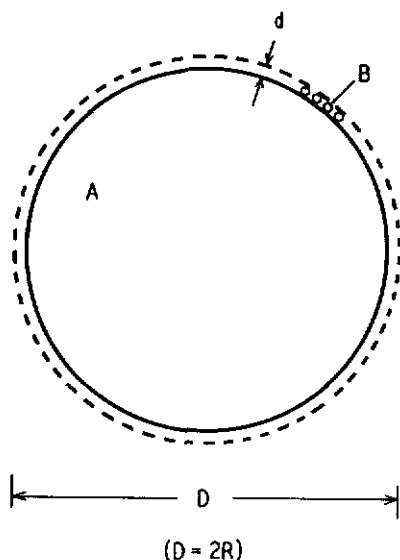
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REFERENCES

1. WHALLEY, V. AND MORELL, S.H. (1973) Powdered Rubbers, Economic and Technological Aspects. *RAPRA Members J.*
2. WOODS, M.E. AND WHITTINGTON, W.H. (1975) Powdered Rubber Technology. *Rubb. Age*, 107, 39.
3. SCHROEDER, H.E. (1975) Powder Processing — A Probable Route to Large-scale Industrial Use. *Proc. 16th IISRP Meet. Rio de Janeiro.*
4. MORELL, S.H. AND PYNE, J.R. (1976) Powders — the Present Position Reviewed. *Eur. Rubb. J.*, 158 (12).
5. LAU, C.M. (1976) Unpublished data. Rubber Research Institute of Malaysia.
6. WONG, S.G. AND LAU, C.M. (1978) Private communication. Rubber Research Institute of Malaysia.

APPENDIX 1  
PARTICLE SURFACE CALCULATIONS



$A$  = Primary particle (rubber)

$B$  = Adsorbed particle (partitioning agent)

Assumptions

1. Both particles are completely spherical.
2. Only unilayer adsorption occurs.
3.  $D \gg d$

To derive an equation relating the weight fractions of  $B$  particles and  $A$  particles; for given sizes and densities of  $A$  and  $B$ .

For any single particle  $A$ :

$$\text{Volume of } A = \frac{4}{3} \pi \left\{ \frac{D}{2} \right\}^3 = \frac{1}{6} \pi D^3$$

$$\text{Weight of } A = \frac{1}{6} \pi \rho_A D^3 \quad \text{where } \rho_A = \text{density of } A.$$

Assuming no voids between the  $B$  particles, the volume of  $B$  covering the total surface area of  $A$ ,

$$= \frac{4}{3} \pi (R + d)^3 - \frac{4}{3} \pi R^3$$

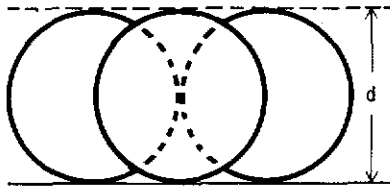
$$= \frac{4}{3} \pi d^3 + 4\pi R d (R + d)$$

$$\approx 4\pi R^2 d \quad \text{if } D \gg d$$

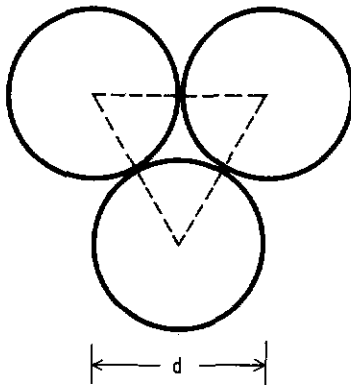
$$\text{i.e. Apparent volume} = \pi D^2 d \quad \text{since } D = 2R$$

However, there are voids between the  $B$  particles, and the ratio of the actual volume of  $B$  particles over the apparent volume is derived as follows.





Side elevation



Plan

Let the area of total surface of

$A$  covered by the  $B$  particles be  $\mathcal{A}$

then number of spheres  $N = \frac{\mathcal{A}}{(\sqrt{3}/4d^2)} \times \frac{1}{2}$

$$\text{i.e. } N = \frac{2\mathcal{A}}{\sqrt{3}d^2}$$

$$\begin{aligned} \frac{\text{Actual volume of spheres}}{\text{Apparent volume of spheres}} &= \frac{N \times \frac{4}{3} \pi \left(\frac{d}{2}\right)^3}{\mathcal{A}d} \\ &= \frac{\pi}{3\sqrt{3}} \\ &= 0.6046 \end{aligned}$$

Hence, taking the voids into account, the volume of  $B$  particles covering each  $A$  particle

$$= \pi D^2 d \times 0.6046$$

Weight of  $B$  particles  $= \pi D^2 d \rho_B \times 0.6046$  where  $\rho_B$  = density of  $B$

$$\text{Weight of ratio of } B \text{ to } A, \phi = \frac{0.6046 \pi D^2 d \rho_B}{\frac{1}{6} \pi D^3 \rho_A} = 3.6276 \left(\frac{\rho_B}{\rho_A}\right) \left(\frac{d}{D}\right)$$