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Stability of Latex-Oil Emulsion Systems

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In the preparation of SMR 5LV and Tyre Rubber, a rubber process oil is added as an emulsion to the latex before the mixture is coagulated. The factors affecting the stability of the oil emulsion and the resultant latex-oil emulsion system have been identified and studied in detail. In a system containing naphthenic oil, the factors affecting the tendency of the oil component to cream are examined.

In the preparation of SMR 5LV and Tyre Rubber, a rubber process oil is added as an emulsion to the latex before the mixture is coagulated. In SMR 5LV production (CHIN, 1967), 4% of the latex rubber is replaced by a naphthenic process oil. In the preparation of Tyre Rubber (CHEONG, 1972; CHEONG SAI FAH AND TI TEOW CHUAN, 1972) a latex-oil emulsion mixture containing 25% by weight of an aromatic or a naphthenic process oil must be made prior to discharge into a bed of wet crumbs obtained from a blend of field coagulum and unsmoked sheets.

In these processes, the latex-oil emulsion system must be sufficiently stable to facilitate its handling in the factory. A stability time in excess of 3 h is desirable. The factors affecting the stability of latex-oil emulsion systems are discussed in this paper.

MATERIALS AND METHODS

Oil Emulsion

In the study of oil emulsion, 33.3 g of the rubber process oil were used. The oil emulsion was prepared in a 150 ml beaker by stirring with a Gallenkemp stirrer, with a three blade plastic propeller, maintained at high speed (speed 10).

Initial studies concentrated on the use of ammonium oleate as the emulsifier. Later on, an alkyl phenol ethylene oxide condensate (APEO) was found to be more effective.

Latex-Oil Emulsion System

In each trial, about 320 ml of latex (100 g d.r.c.) of latex was contained in a 600 ml beaker. The oil emulsion was added to the latex while stirring at low speed (speed 2) over a period of 1 minute. After successful incorporation, the latex-oil emulsion system was observed at regular intervals to detect the onset of coagulation of the system. During the observation period, the system was lightly agitated occasionally to prevent creaming or sedimentation of the oil emulsion.

Creaming

A quantity of the stable latex-oil emulsion mixture was placed in a long graduated glass tube with a discharge at the bottom. Equal samples were removed from the bottom discharge at intervals of 0, ½, 1, 2, 3 and 4 hours. The samples were coagulated at pH 5.2 and the dried rubber tested for acetone extract and Mooney viscosity.

For naphthenic oils, systems containing 4% and 25% of oil were used; for aromatic oil, systems containing 25% oil were studied.

Oil emulsions prepared by high speed mechanical stirring were compared with emulsions prepared by passage through a colloid mill.

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STABILITY OF OIL EMULSION

A good oil emulsion is stable, not too viscous and not too frothy. The stability of the oil emulsion is important since it affects the stability of the resultant latex-oil emulsion mixture. Among other things, the stability of the oil emulsion is dependent on the emulsifier, the formulation and the method of preparation.

Emulsifier

Emulsifiers, suitable for use in latex-oil emulsion systems, should be able to form stable oil emulsions and also should not impede the coagulation of the latex-oil system at low pH, about 5.2. Of the many emulsifiers tested, only ammonium oleate and APEO satisfy both the requirements mentioned.

Ammonium oleate should be formed *in situ* in the oil emulsion. Although ammonium oleate forms stable emulsions with aromatic and naphthenic oils, latex-oil systems containing the aromatic emulsion tend to be more stable than those containing the naphthenic emulsion.

Latex-oil emulsion systems using the APEO as emulsifier tend to be more stable and less sensitive to the pH of the system. APEO forms more stable emulsions with naphthenic than with aromatic oils.

Formulation

The viscosity and density of a rubber process oil are important properties which affect the formulation of the oil emulsion. The typical values for an aromatic and a naphthenic oil are shown in *Table 1*. The stability of the oil emulsion is dependent on its viscosity and the relative density of the oil and water. The viscosity of the oil emulsion increases with the oil viscosity, decreases with increasing water content and increases with increasing ammonium oleate content. *Table 2* illustrates the dependence of oil emulsion stability on these variables.

TABLE 1. VISCOSITY AND SPECIFIC GRAVITY OF RUBBER PROCESS OILS

Item	Aromatic	Naphthenic
Viscosity saybolt at 100°F (seconds)	3000	160
Specific gravity 60/60°F	1.00	0.89

A naphthenic oil, being less dense and less viscous than an aromatic oil, requires less water and a higher ammonium oleate content to form a stable emulsion that has less tendency to cream and separate into two layers. *Formulae 2* and *3* have now been recommended for the preparation of aromatic and naphthenic oil emulsions respectively.

When APEO is used, 1.5 parts per 100 of oil are required for naphthenic emulsions and 2.0 parts for aromatic emulsions. The water content remains the same as for ammonium oleate-based emulsions.

Preparation

The best method of preparing an emulsion is first to mix the oleic acid with the oil; water containing the requisite amount of ammonia is then stirred into the oil-oleic acid mixture *(Table 3)*. In cases where the oleic acid is kept at a minimum (1.0 part), an efficient stirrer can form a good emulsion but this need not lead to a stable latex-oil emulsion system *(Table 4)*. This suggests that an efficient stirrer cannot adequately compensate for a defective formulation. Efficient stirring is important particularly in the preparation of a naphthenic oil emulsion. A well prepared emulsion containing fine oil globules also has less tendency to cream.

STABILITY OF LATEX-OIL EMULSION SYSTEMS

When a stable oil emulsion is added to latex, many factors affect the ability of the latex to accommodate the oil emulsion and the storage stability of the resultant latex-oil emulsion system. Amongst these factors are the pH and stability of the latex, the type and level of oil, the mechanical agitation during incorporation of the oil emulsion and subsequent storages and the type of emulsifier used.

pH and Stability of Latex

For a given type and level of oil, the stability of the latex-oil emulsion system increases with the pH of the latex *(Tables 5*

TABLE 2. DEPENDENCE OF OIL EMULSION STABILITY ON FORMULATION

Chemical	Aromatic oil (parts by weight)				Naphthenic oil (parts by weight)			
	1	2	3	4	1	2	3	4
Oil	100	100	100	100	100	100	100	100
Water	30	40	40	50	20	30	30	40
Oleic acid	1	1	4	1	1	1	2	2
Ammonia	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Viscosity (centipoise)	1 200	350	1 000	160	85	100	700	350
Stability	Good	Good	Good	Poor	Poor	Poor	Good	Poor

TABLE 3. DEPENDENCE OF OIL EMULSION STABILITY ON ORDER OF CHEMICAL ADDITION

Method	Portion A	Portion B	Stability
Add B to A while stirring	Oil + oleic acid	Water + ammonia	Good
Add B to A while stirring	Oil + water	Oleic acid + ammonia	Poor
Stir A	Oil + water + oleic acid + ammonia		Adequate but require efficient stirrer.

TABLE 4. DEPENDENCE OF OIL EMULSION STABILITY ON THE EFFICIENCY OF THE STIRRER

Stirrer	Efficient stirrer			Inefficient stirrer		
Oleic acid	0.5	1.0	1.5	0.5	1.0	1.5
Stability of oil emulsion	Good	Very good	Very good	Poor	Fair	Good
Stability of latex-oil mixture	Very poor	Fair	Good	Very poor	Fair	Good

Emulsion formula: Naphthenic oil = 100, water = 30, ammonia = 0.15, oleic acid = variable as shown in above table.

TABLE 5. EFFECT OF pH OF LATEX AND LEVEL OF OIL ON STABILITY
(Latex-naphthenic oil system)

Item	Rubber: Naphthenic oil (96: 4)			Rubber: Naphthenic oil (75: 25)		
Latex pH	6.5	7.0	7.5	7.5	8.0	8.5
Stability time (h)	0 – 2	2 – 4	3 – 6	0	0 – 4	5 – 6

Note: Stability time is the time lapse before coagulation sets in.

and *6)*. A stable latex which is well preserved in the field tends to give rise to a more stable system *(Table 7)*.

TABLE 6. EFFECT OF pH OF LATEX ON STABILITY
(Latex-aromatic oil system)

Item	Rubber: Aromatic oil (75: 25)		
Latex pH	7.5	8.0	8.5
Stability time (h)	0 – 4	3 – 6	>6

oil emulsion and during storage of the resultant mixture.

A rapid addition of the oil emulsion to the latex promotes the stability of the system *(Table 8)*. A lower speed of the paddle or stirrer will also help to minimise mechanical agitation. A stable system, however, can withstand a considerable amount of agitation *(Table 9)*. Once prepared, the latex-oil emulsion system stores best under static conditions with occasional light stirring.

TABLE 7. EFFECT OF EARLY pH ADJUSTMENT ON STABILITY OF THE LATEX-OIL EMULSION SYSTEM

Item	Rubber: Naphthenic oil (96: 4)		Rubber: Naphthenic oil (75: 25)		Rubber: Aromatic oil (75: 25)	
Latex pH	7.0	7.0	8.5	8.5	8.0	8.0
pH adjusted in[a]	Field	Factory	Field	Factory	Field	Factory
Stability time[b] (h)	2	1	6	2	3	1½

[a]The time lapse between ammonia addition in the field and in the factory is about 4 hours.
[b]The stability time of the latex (without oil) is approximately the same for preservation in the field and at the factory since low levels of ammonia were used.

Level of Oil

A latex-oil emulsion system containing a higher content of oil tends to be less stable. For example, a system containing 25% of a naphthenic oil requires a higher pH of the latex to maintain the same stability as a system containing only 4% oil *(Table 5)*.

Type of Oil

An aromatic oil gives an inherently more stable system than a naphthenic oil. For the same stability time, the pH of the latex can be lower when an aromatic oil emulsion is used *(Tables 5* and *6)*. This is probably due to aromatic oil emulsions being generally more stable than naphthenic oil emulsions.

Mechanical Agitation

The stability of the latex-oil emulsion system can be drastically affected by mechanical agitation during the incorporation of the

TABLE 8. EFFECT OF THE RATE OF ADDITION OF OIL EMULSION ON STABILITY

Item	Naphthenic oil		Aromatic oil	
Latex pH	7.5	7.5	7.5	7.5
Emulsion added over (min)	1	10	1	10
Stability time (h)	3	0	> 3	0

Continuous stirring during storage destabilises the system *(Table 10)*.

Type of Emulsifier

The results and effects described so far relate to an oil emulsion which uses ammonium oleate as the emulsifier. When APEO is used as the emulsifier, the stability of the latex-oil emulsion system is greatly enhanced *(Table 11)*. The use of APEO (Nonidet P40 or Sunaptol OP) makes the system less

TABLE 9. EFFECT OF STIRRER SPEED ON STABILITY

Item	Rubber: Naphthenic oil (75:25)				Rubber: Aromatic oil (75:25)	
Latex pH	7.5	7.5	8.0	8.0	7.5	7.5
Stirrer speed (r.p.m.)	50	500	50	500	50	500
Stability time (h)	1	0	6	6	3 – 5	3 – 5

TABLE 10. EFFECT OF STORAGE CONDITIONS ON STABILITY

Item	Rubber: Naphthenic oil (96:4)		Rubber: Naphthenic oil (75:25)		Rubber: Aromatic oil (75:25)	
Latex pH	7.0	7.0	8.5	8.5	8.0	8.0
Storage conditions	Initial stirring only	Continuous stirring	Initial stirring only	Continuous stirring	Initial stirring only	Continuous stirring
Stability time (hr)	4	½	>4	2	3	1

TABLE 11. COMPARISON BETWEEN AMMONIUM OLEATE AND ALKYL PHENOL-ETHYLENE OXIDE CONDENSATE AS EMULSIFIER

Latex pH	Oil type	Emulsifier (parts)	Stability time (h)
8.0	Naphthenic	Ammonium oleate (1.7)	5
8.5	Naphthenic	Ammonium oleate (1.7)	6
7.5	Naphthenic	APEO[a] (2.0)	>11
8.0	Naphthenic	APEO (2.0)	>11
7.5	Aromatic	Ammonium oleate (1.0)	5
8.0	Aromatic	Ammonium oleate (1.0)	7
7.5	Aromatic	APEO (2.0)	>11

[a]Alkylphenolethylene oxide condensate – Nonidet P40 or Sunaptol OP

TABLE 12. CREAMING OF LATEX-OIL EMULSION SYSTEMS ON STORAGE
(System contains 4% w/w naphthenic oil)

Preparation	Property	Static storage time (h)				
		0	½	1	2	3
Mechanical stirring	Mooney viscosity	61	63	63	61	59
	Acetone extract (% wt)	6.9	6.2	6.3	6.5	7.9
Colloid mill	Mooney viscosity	61	62	61	60	61
	Acetone extract (% wt)	7.0	7.2	6.9	6.7	6.9

sensitive to the pH of latex, the type and level of oil and mechanical agitation. It also does not impede the acid coagulation of the latex-oil emulsion system. This emulsifier should provide sufficient processing safety to justify its use in spite of a slightly higher chemical cost.

CREAMING OF LATEX-OIL EMULSION SYSTEMS

A stable latex-oil emulsion system can become heterogeneous during static storage; this is caused by the tendency of the oil components to cream or to sediment relative to the latex component. This tendency to cream or sediment is dependent on the relative density of the oil and the latex.

Naphthenic oil is less dense than latex. Therefore, a latex-oil emulsion system containing naphthenic oil tends to cream on static storage; the top portion of the latex-oil mixture will tend to be progressively richer in oil content. *Tables 12* and *13* show the change in oil content (measured by acetone extract) of the bottom portion of the latex-oil mixture which is progressively removed from the bottom outlet of the long graduated glass tube holding the latex-oil mixture. Initially (at 0 h) the acetone extract reflects the oil content of the whole bulk. On storage, the oil begins to cream and the acetone extracts of the bottom portions begin to decrease. This is true for the portions removed after ½, 1 and 2 h of storage. At the end of 3 h, the last remaining portion of the latex-oil mixture contains all the oil which has creamed. As expected, this last portion has the highest acetone extract value. These observations confirm that the naphthenic oil does cream rather rapidly. This tendency to cream is particularly pronounced when the oil emulsion is prepared by a mechanical stirrer. This is caused by the rather large size of the oil globules present in the oil emulsion

TABLE 13. CREAMING OF LATEX-OIL EMULSION SYSTEMS ON STORAGE
(System contains 25% w/w naphthenic oil)

Preparation	Property	Static storage time (h)				
		0	½	1	2	3
Mechanical stirring	Mooney viscosity	31	34	36	37	24
	Acetone extract (% wt)	29.2	27.3	26.2	25.3	36.7
Colloid mill	Mooney viscosity	33	34	32	34	32
	Acetone extract (% wt)	27.9	28.0	28.4	27.6	28.3

TABLE 14. CREAMING OF LATEX-OIL EMULSION SYSTEMS ON STORAGE
(System contains 25% w/w aromatic oil)

Preparation	Property	Static storage time (h)				
		0	½	1	2	3
Mechanical stirring	Mooney viscosity	42	43	43	40	43
	Acetone extract (% wt)	28.5	29.0	29.0	30.0	28.0
Colloid mill	Mooney viscosity	42	41	43	43	43
	Acetone extract (% wt)	28.7	29.4	28.9	28.8	28.6

system. Oil emulsions prepared by a colloid mill give finer oil globules. These smaller globules have less tendency to cream because of increased viscous drag. This reduced tendency to cream is evident from the almost constant acetone extracts of the 'colloid mill' samples.

A system containing the aromatic oil emulsion will have less tendency to cream since the density of the aromatic oil is about the same as that of the latex serum *(Table 14)*.

In practice, therefore, it is good to stir the latex-oil mixture intermittently to achieve uniformity in production. This is particularly necessary for systems containing a naphthenic oil.

DISCUSSION

Some of the practical factors affecting the stability of oil emulsions and latex-oil emulsion systems have been studied. The principal factors affecting stability have been identified as the formulation and method of preparing the oil emulsion, the choice of the emulsifier, the pH and stability of latex, and the mechanical agitation of the system. Understanding the influence of these factors has enabled latex-oil emulsion mixtures to be handled satisfactorily in factory processing. The knowledge gained from these studies has been applied to the production of LV rubber and Tyre Rubber.

The APEO (Nonidet P40 or Sunaptol OP) is more effective than ammonium oleate as an emulsifier for latex-oil emulsion systems. Its current high price, however, could reduce its competitiveness.

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