# Chemistry of Breaking of Asphalt Emulsions

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The amount of asphalt emulsion coagulated by contact with different aggregates is determined for a series of soap-stabilized asphalt emulsions. It is shown that the acid action of the stones is not as important in breaking as has so far been supposed. The decisive factor is the reaction between the emulsifier and the calcium ions which are displaced from the stones by contact with the emulsifier solution. The process is not concluded because the stone surfaces are blocked up by coagulated bitumen. The tendency for blockade is dependent on the type of aggregate and on the alkalinity of the emulsion.

• IF AN ASPHALT emulsion is brought into contact with an aggregate, in many cases some of the emulsion will coagulate, even without a simultaneous evaporation of water from the emulsion. This tendency for the emulsion to break in contact with an aggregate can be observed in an experiment by Weber and Bechler (1) in which bitumen coagulates on the stones in such a form that it cannot be removed by rinsing with distilled water. The amount of coagulated bitumen may be determined by weighing.

The measurement of the electrolyte stability of the bituminous emulsions has been used to characterize their breaking qualities. In the measurements (Myer's Test), a known amount of electrolyte, usually calcium chloride, is added to a known amount of emulsion, after which the amount of coagulation of bitumen is measured (2).

By measuring the electrolyte stability, information may be obtained about the quantity of emulsifier (2) or the breaking tendency of salts dissolved in the water on the road (3) and of calcium salts in the aggregate which are soluble in water (4, 5, 6, 7, 8). The importance of the water-soluble salts in the aggregate has been studied by extracting the aggregate with water, adding the extracts to the emulsion, and measuring the coagulation. It has usually been necessary, however, to choose extremely favorable conditions of dissolution (for instance, fine crushing of the aggregates) to obtain a sufficient quantity of salts to determine the coagulating effect of the aggregates.

Because the measurement of the electrolyte stability is a very convenient estimation method, the possibility of a connection between the electrolyte stability and the stability against aggregates has been empirically investigated. The results have been very contradictory: Nasini and Rossi (9) and Bohn and Mikkelsen (10) find good agreement, whereas Statens Vejlaboratorium (11) and Jekel (12), who work with a large number of emulsions, find poor agreement. All these investigators use factory-produced emulsions. McKesson (2) and Neubronner (13), who work with self-produced emulsions, have found very good agreement. However, both have produced their emulsions by varying the amount of the added soap. As the content of alkali in the emulsions is especially important for the breaking qualities (1), it would be reasonable to suppose that more information would be obtained by working with a series of emulsions where the content of alkali is varied, independent of the content of fatty acid.

## WEBER AND BECHLER'S EXPERIMENTS

With a colloid mill four series of potassium oleate-stabilized emulsions are produced. Keppeler, Blakenstein and Borchers (14) have used such a series of emulsions

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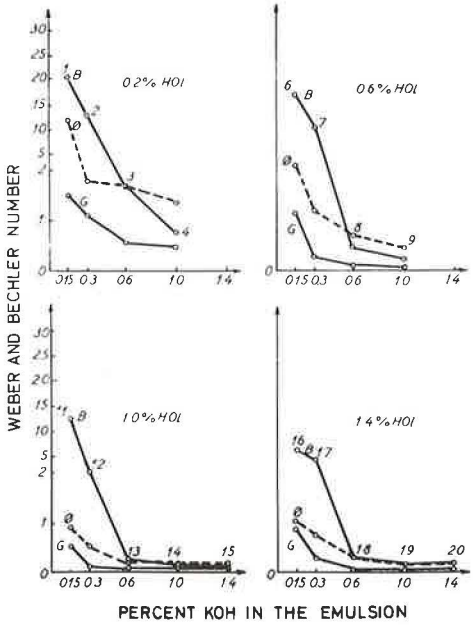


Figure 1. Weber and Bechler numbers (percent coagulated asphalt) for basalt (B), granite (G) and limestone (ϕ).

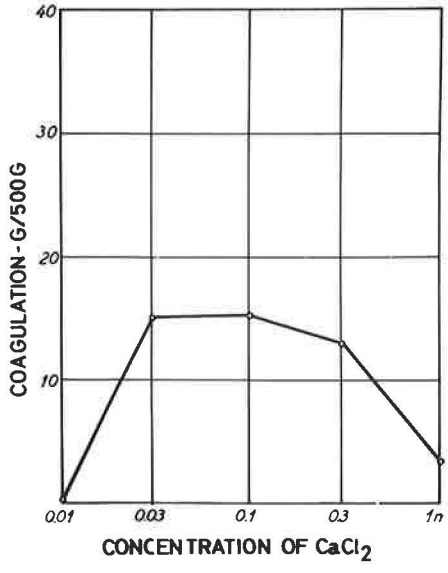


Figure 2. Myers test with 2.2 meq $CaCl_2$ per 500 g Emulsion 8.

for their experiments. All emulsions contained 50 percent bitumen with a penetration of 300. In the first series (Nos. 1 to 5), the content of oleic acid (HOl) was 0.2 percent, and the amount of KOH was 0.15, 0.30, 0.60, 1.0 and 1.4 percent, corresponding to normalities of 0.53, 0.106, 0.21, 0.36 and 0.50, respectively, calculated on the basis of the water phase of the emulsion. The second series (Nos. 6 to 10) contained 0.6 percent HOl; the third (Nos. 11 to 15), 1.0 percent HOl; and the fourth (Nos. 16 to 20), 1.4 percent HOl. Within the last three series, the content of KOH was varied as in the first series. The HOl contents of 0.2, 0.6, 1.0 and 1.4 percent correspond to the normalities 0.014, 0.043, 0.071 and 0.1, respectively, calculated on the basis of the water phase. To this can be added 0.027 from the acid content of the bitumen because the bitumen has an acid number of 1.5. Emulsions 5 and 10 broke immediately after production and were, therefore, omitted from the experiments.

Figure 1 shows the result of Weber and Bechler's experiments with three aggregates: a basalt (B) from the Faroes, a granite (G) from Hammeren in Bornholm, and a limestone (ϕ) from Øland. The figure indicates the amount of bitumen per 100 g aggregate which coagulate in a form that cannot be washed out with distilled water when 10 g of aggregate with the particle size 0.5 to 1 mm is reacted with 50 g emulsion for 1 hour with no evaporation. With increasing content of KOH in the emulsions, the breaking numbers will decrease.

An increase of the content of oleic acid will have the same result, although to a lesser degree. Both phenomena are in agreement with the observations of Keppeler, Blankenstein and Borcher (14).

The basalt numbers are always higher than the granite numbers. Øland limestone normally has a breaking tendency between ability to a higher degree when the content of alkali increases. Therefore, the Øland limestone curves, except for the last series of emulsions, cross the basalt curves as alkali content increases.

## MYER'S TEST

The electrolyte stability has been determined by a modification of Myer's test. To compare it more easily with Weber and Bechler's experiments, 50 g of emulsion was

used, into which 0.22 milliequivalents (meq) calcium chloride solution were added dropwise from a burette with vigorous stirring. It was found that 10 g basalt under certain circumstances will give up this amount of calcium ions. After an hour the emulsion was filtered through a sieve with openings of 0.3 mm, and the coagulate filtered out was washed with distilled water, dried and weighed. The results are referred to 500 g of emulsion as in the Weber and Bechler experiments.

As the results proved to be strongly dependent on the concentration of the calcium chloride solution, the experiments were made with the following addition of solution: 0.22 ml 1 N, 0.73 ml 0.3 N, 2.2 ml 0.1 N, 7.3 ml 0.03 N, and 22 ml 0.01 N. The results are shown in Figure 2. The maximum amount of coagulation occurs at 0.1 N concentration. That the coagulation numbers are low with the weakest calcium chloride solutions agrees with an increase in the electrolyte stability with thinned emulsions (20). The low coagulation numbers with concentrated calcium chloride solutions are due to the coagulation of the bitumen around the single drops of the calcium chloride solution which prevents the effect from spreading in the liquid.

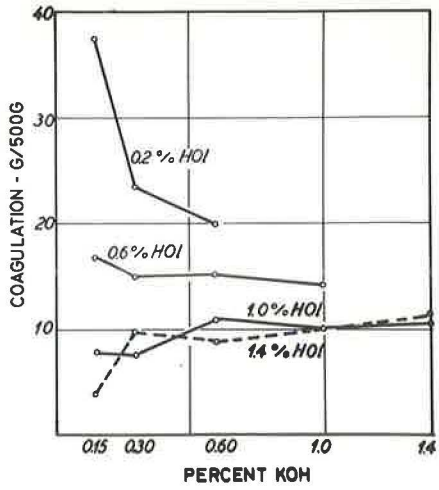


Figure 3. Myers test with $CaCl_2$.

The experiment was carried out with all emulsions at a concentration of 0.1 N. The results (Fig. 3) show that it is essentially the content of fatty acid in the emulsion which determines the stability. Only when emulsions with a fairly constant proportion of KOH to HOl are compared, do increasing Weber and Bechler numbers correspond to increasing Myer numbers.

## ACID ACTION OF AGGREGATES AS BREADING MECHANISM

Williams (15) has shown that even acidic aggregates (that is, aggregates with a high content of $SiO_2$) will not give up hydrogen ions to water. But against alkali hydroxide solutions, most aggregates will work as an acid, and Weber and Bechler (1) have found the breaking to be due to the acid action of the stones. If an active stone was put into potassium hydroxide, the activity of the stone was considerably reduced. They explained this by the fact that the acid action of the stone (as they call it, the alkali adsorption ability) is neutralized. Furthermore, the stability of an emulsion is increased by addition of potassium hydroxide. Keppeler, Blankenstein and Borchers (14) state that if an active aggregate is put into a soap solution, the latter becomes turbid, probably due to precipitated fatty acid. They have also measured the acid action for a series of stones and have found good agreement between the acid action and the breaking numbers. Klinkmann (7) has proposed a theory according to which the alkali concentrates at the stone surface, causing the emulsifier soap to be salted out, resulting in coagulation. The alkali is bound, however, in the formation of salt, and as Nasini and Rossi (8) have pointed out, Weber and Bechler's alkali-treated stones give especially small breaking numbers. Nasini and Rossi also find rather good agreement between the acid action and the breaking ability of the stones; however, they do not see the acid action as the actual cause for breaking. Rather, without any experimental basis, they see the cause as the adsorption of sodium ions on the stone surface, resulting in a disturbance of the balance in the electric double layer.

## STABILITY AGAINST ACIDS

As the acid action of the stones is said to be important, the stability of the emulsions against acids is determined by performing Myer's test with acetic acid. An amount of

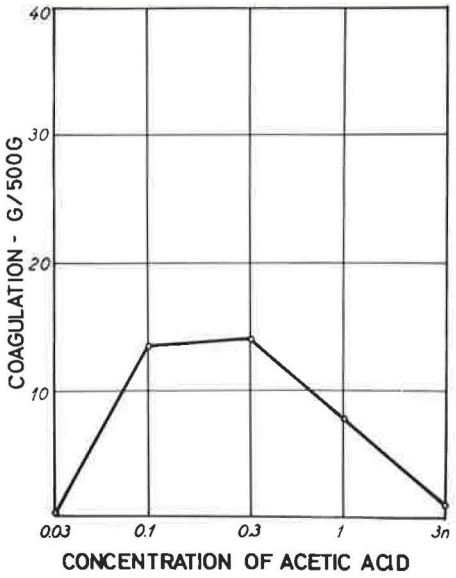


Figure 4. Myers test with 2.2 meq acetic acid per 500 g emulsion.

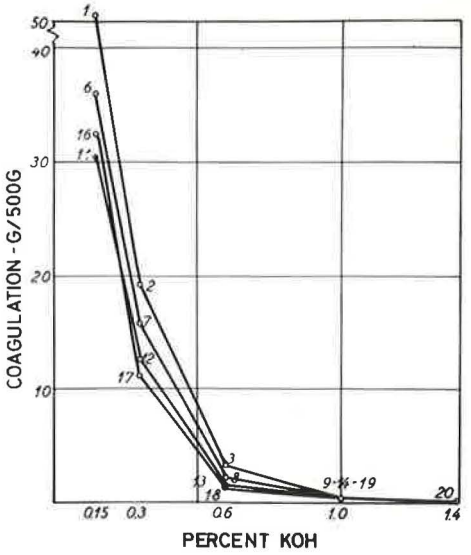


Figure 5. Myers test with acetic acid.

0.36 meq acetic acid was added in the form of 0.03, 0.1, 0.3, 1 and 3 N solutions to 50 g of Emulsion 12. As mentioned later, 0.36 meq is the amount of hydrogen ions which 10 g of basalt can give up under certain circumstances. The coagulation numbers shown in Figure 4 are quite similar to those for addition of calcium chloride (Fig. 2). The experiment was carried out using the emulsions at a concentration of 0.1 N. The results (Fig. 5) show good agreement with the Weber and Bechler numbers for basalt (Fig. 1). Again it is observed that the stability increases greatly when the content of potassium hydroxide in the emulsifier increases, whereas the stability increase with increase in oleic acid is more modest. The results differ greatly from the calcium chloride numbers in Figure 3.

## DIFFICULTIES IN ACID-ACTION THEORY—CATION EMULSIONS

The measurements of the stability against H ions and Ca ions were in rather good agreement with Weber and Bechler (1) and Keppeler, Blankenstein and Borchers (14), suggesting that the acid action of the stones is decisive for breaking. There are, however, many phenomena which cannot be explained by the acid-action theory. For example, the Weber and Bechler experiments showed that the examined limestone usually was more stable than basalt in emulsions rich in alkali, whereas the opposite was true in emulsions poor in alkali. Also, Weber and Bechler have found that the ranking of breaking for a series of stones was dependent on the emulsion. These findings show that the acid action of the stones cannot alone be responsible for the breaking action.

Myer's experiment with HAc indicated that 3.6 ml 0.1 N HAc coagulated 36 g bitumen per 500 g emulsion when Emulsion 6 was used. This is more than, though of the same order of magnitude as, the Weber and Bechler number for basalt (17). Experiments with addition of 3.6 ml 0.1 N boric acid and 3.6 ml of a 0.1 N suspension of aluminum hydroxide, gave, however, the very small coagulation numbers of 0.23 and 0.13 g per 500 g emulsion, respectively. The acid-action theory thus forces us to conclude that the stone looked upon as an acid is almost as strong as acetic acid; this does not sound very probable.

The breaking process cannot be explained by the acid action of the aggregate in acidic cation emulsions. These emulsions come outside the scope of this investigation. Some experimental results will, however, be mentioned for a 50 percent emulsion made with bitumen 300 as binder and 1.3 percent cetyl pyridium chloride as emulsifier. The

TABLE 1

ACID ACTION OF BASALT AND GRANITE

| KOH (N) | Basalt (meq/100g) | Granite (meq/100g) |
|---|---|---|
| 0.3 | 5.1 | 0.46 |
| 0.1 | 3.63 | 0.35 |
| 0.03 | 2.11 | 0.23 |
| 0.01 | 1.11 | 0.19 |

emulsion had a pH of 5.6, and Weber and Bechler numbers of 6.5 and 1.6 were measured against basalt and granite, respectively.

Basalt and granite work as acids (against alkalis.) However, against acids they work as bases. The base action was measured under conditions corresponding to a Weber and Bechler experiment by pouring 50 ml 0.05 HCl over 10 g stone with the particle size 0.5 to 1.0 mm. After an hour the glass was inverted several times, and after centrifuging for 5 min, 25 ml was pipetted. After titration and deduction of the acid consumption in a control experiment, the result was indicated as milliequivalents OH per 100 g aggregate. For basalt and granite the base action was found as 2.67 and 0.73 meq/100 g, respectively.

If the KOH concentration is varied, the acid actions obtained (40 g 0.5 to 1 mm crushed stone in 100 g KOH for 1 hr) are as given in Table 1.

The most alkaline of the emulsions is Emulsion 15. The water phase has a KOH surplus corresponding to a concentration of approximately 0.4 N. The acid action decreases rather considerably at low concentrations. The acid action was correspondingly measured by pouring 50 ml 0.05 N KOH over 10 g stone. For basalt and granite the acid action was 3.02 and 0.39 meq/100 g, respectively.

In the same way as an anion soap-stabilized emulsion breaks on addition of acid, a cation soap-stabilized emulsion will break on addition of alkali. Vogt (16) has found that pH increases on addition of certain kinds of stone to an amine salt solution. The coagulation occurring simultaneously is larger, however, than the coagulation occurring on addition of an amount of ammonia corresponding to the base action of the stone. Vogt explains the breaking of the cation soap emulsions by a completely physical adsorption of the amine salt to the stone surface.

Calculation shows that an emulsion containing 0.2 percent oleic acid has 6 times as much oleic acid as is necessary for covering the emulsion drops, the average diameter of which is 2 $\mu$ with a monomolecular layer of oriented oleate ions.

The breaking by contact with aggregates can not be explained by the fact that these adsorb a monomolecular layer of oleate and thereby deprive the emulsifier films of their oleate ions because the specific surface of the aggregates is small in a surface treatment.

Fuerstenau (17) has studied the adsorption process by measuring flow potentials for the combination $SiO_2$-amine salt solution. He thinks that it is possible to explain certain bends in the zeta potential curve by assuming that at these concentrations, which are about a hundred times smaller than the critical concentration for the formation of micelles (CMC), "hemimicelles" are built at the quartz wall. Below this concentration, the amines are adsorbed one by one. This strong adsorption of amine salts to $SiO_2$ supports Vogt's theory of the amine salt adsorption of the stones as the cause for breaking.

## CONTENT OF EXCHANGEABLE IONS IN STONES

Aqueous extracts of aggregates have, as earlier mentioned, only little coagulating action. However, the water phase in the emulsion holds electrolytes, and it would, therefore, be appropriate to examine the number of coagulating ions which can be displaced by treating the stones for 1 hr with different electrolytes. $NH_4Cl$ or KCl was initially used as the electrolyte, and test conditions were relatively simple. The same exchanges are used in agricultural chemistry. Calcium was determined by titration with complexone by the method of Hildebrand and Reilley (18), and calcium + magnesium was determined by the method of Diehl, Goetz and Hach (19), who also used complexone. For basalt and granite, the Ca + Mg numbers were only about 10 to 15 percent higher than the Ca numbers.

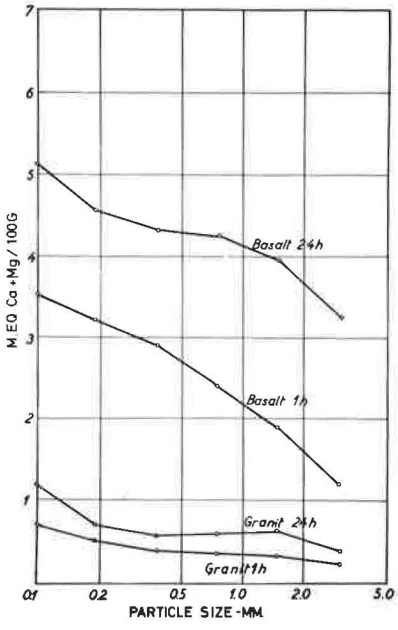


Figure 6. Dependence of displacement of Ca + Mg ions in $NH_4Ac$ on size of aggregate.

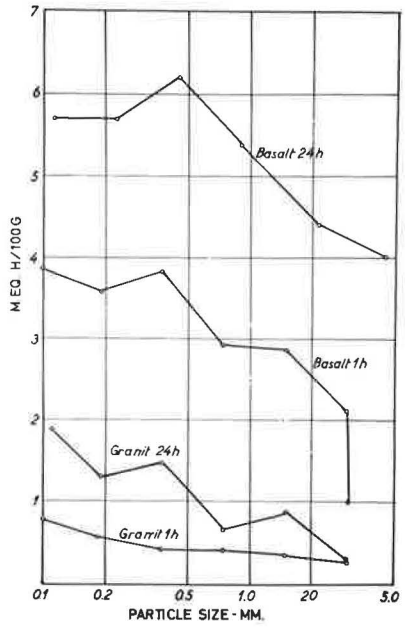


Figure 7. Dependence of acid action in KOH on size of aggregate.

Figure 6 shows the results of a series of experiments with granite and basalt in terms of the number of milliequivalents Mg + Ca ions displaced by the reaction between 100 g stone and 500 ml 0.1 N ammonium acetate at reaction times of 1 and 24 hr. Astonishing large amounts of Mg + Ca are dissolved; for example, for basalt with the particle size of 1 mm in a reaction time of 1 hr, 2.2 meq, the amount chosen in Myer's experiments, are dissolved. The ion exchange increases with increasing surface area, but by less than what would correspond to proportionality. Increasing the time from 1 to 24 hr increases the ion exchange 50 to 100 percent. Basalt is seen to be 4 to 6 times more active than granite.

Figure 7 shows the acid action measured in milliequivalents ions per 100 g stone after 1- or 24-hr reaction with 0.05 N KOH. The numbers are a little higher than the Ca numbers; for basalt with the particle size of 1 mm and with a reaction time of 1 hr, the acid action is 3.6 meq, the amount chosen in the earlier mentioned Myer's experiments with acetic acid.

Weber and Bechler's experiments have been made with the same aggregates and Emulsion 6. The result is seen in Figure 8. The curves are similar to the ion exchange curves, but the importance of the particle size is greater, without, however, reaching proportionality between surface and coagulation numbers. This is consistent with the observation of Martin and Hermann (20) that the coagulating tendency of soap-stabilized emulsions is rather low on small additions of electrolytes and then rises disproportionately strongly on larger additions of electrolytes. The Weber and Bechler numbers for 1 mm basalt are of the same order of magnitude as the earlier ascertained coagulation numbers on addition of 2.2 meq Ca or 3.6 meq H ions. However, it must be pointed out that the 3.6 meq H ions have been determined against an extraction liquid which was 0.05 N with regard to OH ions—Emulsion 6 does not contain that many OH ions.

With basalt of the particle size 0.5 to 1 mm, an experiment was conducted where the $NH_4Ac$ concentration in the exchange liquid was varied from 1 to 0.05 N. The experiment showed that the amount of Ca + Mg exchanged during 1 hr decreased from 4.3 to 1.6 meq/100 g.

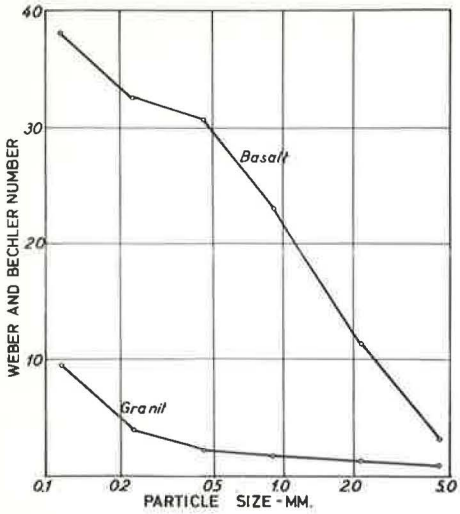


Figure 8. Dependence of Weber and Bechler numbers (percent coagulated asphalt) on particle size.

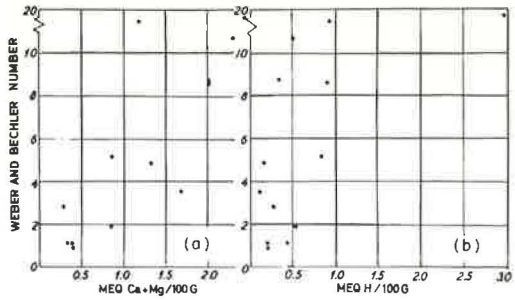


Figure 9. Dependence of Weber and Bechler numbers on (a) amount of exchangeable Ca + Mg ions and (b) amount of H ions.

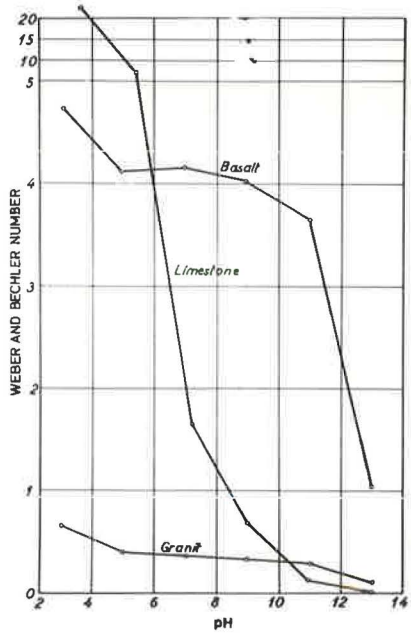


Figure 10. Dependence of Ca ion exchange on pH of exchange solution (KCl).

If the concentration of $NH_4Ac$ is chosen as 0.1 N, and the proportion between the amounts of basalt and ammonium acetate solution is altered from 2:100 to 50:100, then the exchanged amount of Ca + Mg decreases from 3.37 to 2.49 meq/100 g. In a Weber and Bechler experiment, the ratio of stone to serum is 20:100. The observations are in agreement with those found in agricultural chemistry.

In Figure 9, the Weber and Bechler numbers are plotted for Emulsion 6 in reaction with 13 aggregates (four granites, four limestones, one diabase, one slate, one sandstone, one cleave stone and one basalt). In Figure 9a the Weber and Bechler numbers are plotted against the milliequivalents of Ca + Mg ions displaced by reaction for 1 hr with 0.1 N $NH_4Ac$, and in Figure 9b they are plotted against the milliequivalents of H ions removed by reaction for 1 hr with 0.05 N KOH. The correlation between Weber and Bechler numbers and ion exchange is bad, especially for the acid-action numbers. There seems to be no correlation between the mineralogical composition of the stones and the breaking ability. The limestones all give up rather large amounts of Ca + Mg ions, whereas the acid action generally is small.

Measurements are made with the 13 aggregates to see how many coagulating ions are dissolved in distilled water alone. An average of only 22 percent of the amount of Ca + Mg were found by reaction for 1 hr with $NH_4Ac$.

Figure 10 shows the pH dependence of the Ca ion exchange for Hammer granite, Faroe basalt and Øland limestone. As exchange liquid, 1 N KCl is used, with pH regulated by additions of HAc, $NH_4Ac$, or KOH or mixtures of these. The calcium exchange falls with increasing pH. It is strange that the fall is extraordinarily great for Øland

TABLE 2

AMOUNTS OF CALCIUM AND MAGNESIUM IONS DISPLACED IN 0.05 N POTASSIUM OLEATE

| KOH Surplus (%) | pH | Ca+Mg (meq/100g) | | |
|---|---|---|---|---|
| | | Granite | Basalt | Limestone |
| 0 | 9.6 | 0.18 | 1.03 | 0.23 |
| 10 | 10.1 | 0.17 | 1.08 | 0.24 |
| 30 | 11.1 | 0.17 | 0.90 | 0.20 |
| 100 | 11.9 | 0.11 | 0.79 | 0.17 |

TABLE 3

REACTIONS BETWEEN BASALT FILLER AND SOAP SOLUTION

| Alkali Surplus (%) | pH Before Exper.[a] | pH After Exper.[a] |
|---|---|---|
| 0 | 9.6 | 8.5 |
| 10 | 10.1 | 9.3 |
| 30 | 11.1 | 9.9 |
| 100 | 11.9 | 11.2 |

[a]Addition of basalt filler.

limestone, as this stone showed relatively large Weber and Bechler numbers in emulsions rich in alkali. Mattson and Larrson (21, p. 129) have determined by using bentonite that Ca is bound more strongly than $NH_4$ with increasing pH, which agrees with the results shown in Figure 10.

## REACTIONS BETWEEN STONE AND SOAP SOLUTION

The Ca and Mg exchange was determined by letting 40 g 0.5 to 1 mm crushed stone react for 1 hr with 100 ml 0.05 N potassium oleate (KOl). The liquid was then decanted off and the crushed stone was rinsed with distilled water. The Ca + Mg ion content of the decanted liquid and the rinsing water was determined by the method of Leggieri (22), that is, by boiling the Ca + Mg soaps with hydrochloric acid, filtering off the oleic acid, and titrating the filtrate with complexone. To facilitate filtering off of the oleic acid a mixture of 25 percent stearic acid and 75 percent oleic acid was used for the experiment instead of pure oleic acid. This method could not be used with Øland limestone because small particles of limestone came into the rinsing water and resulted in calcium numbers which were too large. Therefore, the Ca oleate amount was determined turbidimetrically in a colorimeter by Lange's method.

The results of these determinations are given in Table 2. The amounts of Ca + Mg ions displaced in 0.05 N KOl is a little smaller than earlier found in 0.05 N $NH_4Ac$. The small amount of exchange, in spite of the poor solubility of the calcium oleate, may be because the potassium ions are bound in the ion atmosphere around the micelles, which diminishes their ability to displace Ca ions. It is also found that the exchange decreases with increasing pH, especially when considering that a 0.05 N KOl solution with 100 percent KOH surplus is 0.1 N with regard to K ions and, therefore, judging from the results with $NH_4Ac$, should give 1.5 times more Ca + Mg than 0.05 N KOl without any surplus of KOH.

As mentioned earlier, Keppeler, Blankenstein, and Borchers (14) declare that the turbidity which may be observed in a soap solution on reaction with an aggregate is due to precipitated fatty acid. This obviously cannot be correct: the precipitate must at any rate partly consist of calcium soap. To clear up this problem, 40 g aggregate, 0.5 to 1 mm, was again reacted for 1 hr with 0.05 N KOl. The stones were removed and rinsed, and the soap water and rinsing water were evaporated to dryness on a steam bath. The residue was extracted with boiling 96 percent alcohol, and the fatty acid was titrated potentiometrically with a glass electrode to pH 10. A control experiment was conducted without addition of stone. Results in milliequivalents per 100 g were 0.09 fatty acid and 1.03 Ca + Mg for basalt, no fatty acid and 0.18 Ca + Mg for granite, and -0.48 fatty acid and 0.23 Ca + Mg for limestone. This shows that in a reaction between a KOl solution and aggregate, only small amounts of fatty acid are disengaged, compared with the amount of Ca + Mg oleate precipitated. Øland limestone even binds fatty acid.

If 40 g basalt filler (particle size less than 0.076 mm) is added to 100 g 0.05 N KOl, pH decreases an average of 0.9 after 1 hr (Table 3).

## EXPERIMENTS WITH AGGREGATES SUBJECTED TO CATION EXCHANGE

Table 4 indicates the result of measurements of acid action in KOH, Ca and Ca + Mg exchange in $NH_4Ac$, and Weber and Bechler numbers for Emulsions 6 and 8 in reaction with basalt which has been subjected to different cation exchange treatments. Calcium chloride treatment consisted of placing 200 g basalt in 0.5 liter 1N $CaCl_2$ for 30 min, then replacing the $CaCl_2$ solution with fresh solution. This is repeated seven times. The basalt was rinsed ten times for 15-min periods with 1 liter distilled water each time until the rinsing water was free of chloride. Then the stones were dried. Table 4 indicates that, whereas the Ca + Mg numbers have increased 20 percent, the Weber and Bechler numbers and the acid action are almost unaltered by the treatment.

The procedure with KOH was the same as that just described with $CaCl_2$; it was, however, necessary to use 5 N instead of 1 N solution to passivate the stones sufficiently. With the treatment, the acid action and the contents of Ca and Ca + Mg are reduced to approximately 20 percent of the original value. The Weber and Bechler numbers obtained with both emulsions are very small.

This experiment has produced both a reduction of the acid action of the stones on accountof the added OH ions and an exchange of the bivalent metal ions with monovalent ions. Therefore, there is a special interest in the next experiment, in which the basalt is treated with 1 N NaCl. The Na ions have a greater ability for ion exchange with the hydrogen ions of the aggregate than do the Ca ions; the acid action decreases to about half the original value. This is still a rather considerable acid action, and it is, therefore, surprising that the Weber and Bechler numbers are now practically zero. This should be a strong argument against the acid action theory.

The content of Ca + Mg is reduced still more than in the alkaline exchange liquid in the previous experiment. This is in agreement with the results of the measurement of the dependence of the exchange in KCl on pH: the Ca ions had relatively little tendency to be exchanged by monovalent cations at high pH.

An unsuccessful attempt was made to neutralize the acid action of the basalt by treating with $Ca(OH)_2$. In saturated $Ca(OH)_2$ solution, the OH ion concentration is so small that there is little reduction of acid action. The high Ca + Mg numbers show once more that Ca is strongly bound at high pH.

When basalt was treated with $MgSO_4$, the Weber and Bechler numbers were not very high; indeed, for Emulsion 8 the number was zero. The reason for this is that Mg in the emulsion containing OH ions is precipitated as $Mg(OH)_2$ which is less soluble than $MgOl_2$.

When basalt was treated with 1 N acetic acid (hydrochloric acid corrodes basalt strongly), the content of exchangeable Ca ions was reduced to 16 percent of the original value. At the same time the acid action increased so that H + Cawas about the same as before treatment. The Weber and Bechler numbers for Emulsion 6 were rather high.

TABLE 4

CATION EXCHANGE TREATMENTS OF BASALT

| Treatment | H (meq/100g) | Ca (meq/100g) | Ca + Mg (meq/100g) | Weber and Bechler No. | |
|---|---|---|---|---|---|
| | | | | Emul. 6 | Emul. 8 |
| None | 3.12 | 2.29 | 2.63 | 19.1 | 0.85 |
| $CaCl_2$ | 3.33 | 3.17 | 3.17 | 20.70 | 0.85 |
| NaOH | 0.62 | 0.51 | 0.55 | 0.82 | 0.02 |
| NaCl | 1.42 | 0.064 | — | 0.19 | 0.02 |
| $Ca(OH)_2$ | 2.18 | 4.25 | 4.31 | 18.9 | 2.65 |
| $MgSO_4$ | 4.43 | 0.25 | 2.95 | 18.0 | 0 |
| HAc | 4.80 | 0.37 | — | 13.61 | 0.17 |

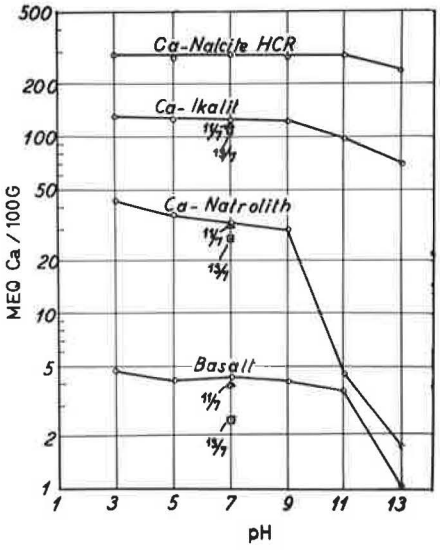


Figure 11. Dependence of Ca ion exchange on pH of exchange solution.

The hydrogen ions taken up by exchange were rather loosely bound in contrast to those after treatment with NaCl. The amount of fatty acid disengaged by the reaction between basalt treated with HAc and soap solution was also rather high, 0.80 meq/100 g, as compared with 0.09 meq/100 g for untreated basalt. The Weber and Bechler number for Emulsion 8 is very low. Emulsions rich in alkali are not sensitive to aggregates with great acid action when the content of the stones of exchangeable Ca ions is small.

## EXPERIMENTS WITH WATER-SOFTENING ION EXCHANGERS

Some experiments were made with three anion exchangers with large exchange capacities. Figure 11 shows the pH dependence of the ion exchange expressed as milliequivalents Ca displaced by the reaction for 1 hr with 1N KCl for three water-softening ion exchangers in Ca form; the earlier measured numbers for basalt are indicated for comparison. The ion exchangers used were Nalcite HCR, an ion exchange resin produced by Dow Chemical Corp.; Natrolith, a product produced by burning an ion exchanging clay from Sweden; and Ikalit, a tuff from Iceland. Because of the high ion exchange capacities, only 2 g Natrolith, 0.2 g Nalcite HCR, and 0.6 g Ikalit were used with 100 g 1N KCl to determine ion exchange.

The curves show that the exchange capacities of the water-softening ion exchangers are up to 75 times greater than that of basalt, and also that the decrease of the exchange capacities with increasing pH is very different: quite small for Nalcite HCR, larger for Ikalit and much larger for Natrolith. The great decrease of the exchange ability might perhaps be due to a destruction of the material in the strongly alkaline liquids. The points marked 11/7 and 13/7 show the ion exchange in materials exposed for half the time to the influence of the exchange liquid at a pH of 11 and 13, respectively, and half the time at a pH of 7. Even the 13/7 points are not very much lower than the curves; therefore, destruction of the materials at high pH cannot be the main cause for the decrease of exchange capability.

In Table 5, the acid action, the Ca exchange and the Weber and Bechler numbers against Emulsion 7 for the anion exchangers are given. For the Ca form of the inorganic

TABLE 5

PROPERTIES OF WATER-SOFTENING ION EXCHANGERS

| Ion Exchangers | H in 0.05N KOH | Solid/100 ml Liquid (g) | Ca in 1N KOl | Ca in 0.1N $NH_4Ol$ | Solid/100 ml Liquid (g) | W-B No. Emul. 7 |
|---|---|---|---|---|---|---|
| Ca-Natrolith | 22.2 | 4 | 32 | 18.7 | 2 | 31.8 |
| Ca-Nalcite | 6.5 | 12 | 299 | 89 | 0.2 | 7.24 |
| Ca-Ikalit | 65.4 | 1.2 | 126 | — | 0.6 | — |
| Basalt | 3.12 | 40 | 4.4 | 2.63 | 40 | 14.8 |
| H-Nalcite | 143 | 1.5 | — | 0.14 | 2 | 57 |
| K-Natrolith | 8.3 | 4 | — | 0.9 | 2 | 0 |

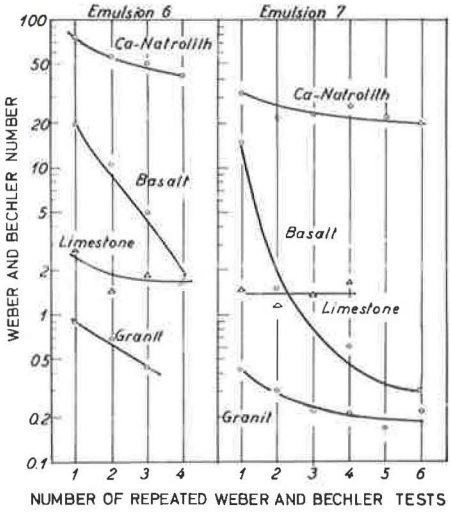


Figure 12. Blocking of stone surfaces by coagulated asphalt restrains ion reactions.

ion exchangers, the proportion between acid action and Ca exchange is nearly the same as for basalt, whereas the ion exchange resin Nalcite HCR has a minimal acid action considering the great ion exchange capacity. Wiklander (21, p. 138) mentions that the ranking of the displacement ability of the ions will be Ca > K > H for ion exchangers containing strong acid groups such as Nalcite HCR; this is in agreement with the fact that the acid action is small in Nalcite HCR when treated with $CaCl_2$. For ion exchangers with weaker acidic qualities, such as the inorganic ion exchanger Permutit, the ranking changes to K < Ca < H, which agrees with the facts that there still existed a great acid action in Natrolith and basalt after treatment with $CaCl_2$, and that a small Ca content existed in the basalt treated with acetic acid. However, it does not agree with Wiklander's experiences that the acid action for basalt and, as later shown, for Natrolith is reduced by treatment with alkali metal chloride, whereas it is not reduced by treatment with calcium chloride.

The Weber and Bechler numbers for Ca-Natrolith are only about twice the numbers for the basalt, although its ion exchange numbers and acid action are many times greater than that of the basalt. Also, Ca-Nalcite shows astonishingly small Weber and Bechler numbers, especially when considering its low specific weight. Ca-Nalcite has a relatively small acid action; therefore, a sample was made of H-Nalcite by leaching with hydrochloric acid; it had a great breaking ability. The superior breaking ability of H-Nalcite agrees with the previously mentioned displacement ranking: it is easier for the K ions of the emulsion to displace H ions than Ca ions.

The K-Natrolith in Table 5 was produced by leaching Ca-Natrolith with KCl. The acid action decreased considerably as in the earlier mentioned corresponding basalt experiment, whereas the Weber and Bechler number decreased to about zero as a consequence of the exchange.

Unfortunately, Ikalit proved to be unfit for determination of the Weber and Bechler numbers, losing all its strength and crumbling away due to drying out.

## BLOCKING OF STONE SURFACES

Figure 12 shows the result of a series of Weber and Bechler number determinations on the same aggregate with Emulsions 6 and 7, in which the aggregate was rinsed free from bitumen with benzene in between the experiments. The Weber and Bechler number was 19.1 for Emulsion 6 and untreated basalt, in which the content of Ca ions exchangeable in 0.1 N $NH_4Ac$ and the acid action against 0.05 N KOH were 2.63 and 3.12 meq/100 g, respectively. After the coagulated bitumen was removed, a Weber and Bechler number of 10.4 was measured on the same aggregate. This was repeated four times. The Weber and Bechler number decreased to only 1.8 after the fourth experiment. If the stones were again rinsed with benzene, 0.24 and 1.18 meq/100 g would be found for the exchangeable Ca ions and the acid action, respectively. In the experiments with Emulsion 7, which is richer in alkali, the Weber and Bechler number decreased still more with the number of experiments. At the same time the content of exchangeable Ca ions and the acid action decreased to 0.58 and 0.52 meq/100 g, respectively, after the sixth experiment. The Ca exchange occurs slower in the more alkaline emulsion; this agrees with the earlier mentioned dependence of the Ca exchange on pH.

The Øland limestone behaves quite differently from basalt: the breaking numbers change little in the repeated Weber and Bechler experiments, and the amount of Ca dis-

solved in $NH_4Ac$ also stays constant. Whereas basalt has a breaking action in these experiments until the exchangeable Ca ions are used, the breaking ability of the Øland limestone will not change. The reaction between soap solution and aggregate does not have the character of ion exchange here.

Granite shows small Weber and Bechler numbers which decrease on repeating the experiments, as do the basalt numbers, but at a somewhat slower rate.

The Weber and Bechler numbers for Ca-Natrolith are high, but not as high as expected from the great ion exchange capacity because the coagulated bitumen also blocks up the stone surfaces. The Ca and H numbers decrease less with the number of experiments than in the case of basalt: from 18.9 and 22.2, respectively, for untreated Ca-Natrolith to 15.0 and 17.3 after the fourth Weber and Bechler experiment with Emulsion 6 and to 9.8 and 13.1 after the sixth experiment with Emulsion 7.

It may be added that the Weber and Bechler numbers are only increased by 8 percent when the time in the Weber and Bechler experiment with Emulsion 7 and basalt is increased from 1 to 4 hr, so that the facts shown on the curve cannot be explained by a longer reaction time.

## ADHESION BETWEEN STONE AND BINDER—CONCLUDING REMARKS

From the preceding experiments, it appears that there is no simple connection between the ion exchange and the Weber and Bechler numbers. At most, a connection might be expected between the ion exchange and the amounts of bitumen coagulated in many repeated Weber and Bechler experiments accumulated by benzene extraction. That would be a very time-consuming operation and would have very little relation to what happens in practice.

The blocking-up of the stone surfaces with coagulated bitumen is closely connected with the problem which is highly discussed in the asphalt literature: the adhesion between asphalt bitumen and wet aggregates. Riedel and Weber (23) have tried to measure the adhesion by visually judging the displacement of bitumen from the stone surface on boiling with water. If the aggregate-bitumen combination passed this test, an attempt was made to use a displacement liquid with better wetting properties than water. Riedel and Weber repeated their boiling test with a series of soap solutions with increasing concentration, and used the concentration of the soap solution which just could displace the bitumen from the stone as a measure for the adhesion. Later Riedel and Weber found out that the differentiation became better when using a series of soda solutions with increasing concentrations. These experiments indicated that aqueous alkali solutions will more thoroughly prevent the contact of the stone-binder with a more alkaline solution.

This is certainly the cause contributing most highly to the decrease of breaking numbers in very alkaline emulsions. In the emulsions rich in alkali, the bitumen particles will be kept away from the stone surfaces. Therefore, the Ca ions displaced by ion exchange must preferably react to make insoluble Ca soap with the fatty acid ions which have not been adsorbed on the bitumen drops, but are distributed molecularly dispersed or as micelles in the dispersing medium. The decrease of the breaking with increasing alkalinity is supported by the fact that the Ca ion exchange decreases with increasing pH.

In emulsions with smaller alkalinity, the repulsion between the bitumen drops and the stone surface will be less, so that the Ca ions displaced by ion exchange will be able to precipitate Ca soap from the fatty acid anions which have been adsorbed on the bitumen drops. This may be counteracted to some extent by increasing the amount of fatty acid in the emulsion; the emulsions rich in fatty acid also proved to be more stable than the emulsions poor in fatty acid.

The earlier found correspondence between breaking and acid action is due to the fact that many aggregates (but not limestone) with high acid action also possess many exchangeable Ca ions. The experiments with basalt treated with NaCl and Natrolith treated with KCl show, however, that it is possible to make aggregates which, in spite of a rather high acid action, have a small breaking activity. By the alkali chloride treatment, the acidic action decreased somewhat; some of the most easily exchangeable hydrogen ions must have been displaced. The remaining hydrogen ions are bound so

TABLE 6

ADHESION TENSION MEASUREMENTS

| Aggregate | Treatment | P (cm $H_2O$) | p (cm $H_2O$) | A (dynes/cm) |
|---|---|---|---|---|
| Basalt | Untreated | 55.3 | 9.0 | 11.7 |
| | NaCl completely | | 1.25 | 1.6 |
| | NaOH completely | | < 0.5 | < 0.6 |
| | NaOH partly | | 4.5 | 5.8 |
| Granite | Untreated | 60.8 | 7.5 | 8.9 |
| | NaCl completely | | 0.75 | 0.9 |
| | NaOH completely | | < 0.5 | < 0.6 |
| | NaOH partly | | 4.5 | 5.3 |
| Øland limestone | Untreated | 63.9 | 11.5 | 13.0 |
| | NaCl completely | | 11.5 | 13.0 |
| | NaOH completely | | 9.5 | 10.8 |
| | NaOH partly | | 10.0 | 11.2 |

strongly that they have not been able to disturb the hydrolysis balance of the soap sufficiently to cause coagulation.

Some of the hydrogen ions in the ion exchange resin Nalcite HCl treated with hydrochloric acid are bound so loosely that there is a certain breaking ability although the content of exchangeable Ca ions is zero.

It would be interesting to be able to judge the adhesive ability between asphalt bitumen and stone in contact with a soap solution. In the English immersion tray test (24), water (in this case, soap solution) is poured onto a layer of asphalt. A stone is put through the layer of water and pressed into the layer of asphalt. After 5 min the stone is removed and it is visually assessed if the stone is wetted with asphalt. An experiment with 0.5 to 1 mm stones, fixed by a small pair of tweezers, shows that all aggregates, with exception of the ion exchange resin Nalcite HCR (both H-, Ca-, and K-Nalcite), have insufficient adhesion. However, Nalcite showed the greatest disproportion between a great ion exchange capacity and a relatively small Weber and Bechler number.

The adhesion of the aggregates which did not pass this test (that is, basalt, granite and Øland limestone) was examined by the Bartell-Halberg displacement cell (25). The principle here is that a column of stone powder with a particle size of 0.10 to 0.15 mm is soaked with 67 percent solution of bitumen 300 in mineral turpentine with a viscosity of 225 cP at 25 C. After 15 min a certain minimal water pressure, p, in dynes per square centimeter is applied to attempt to displace the binder with water. The experiment is repeated with the stone column soaked with water, and a measurement is taken of the air pressure, P, which is just sufficient to displace the water from the stone column. Because the surface tension of the water is 72 dyne/cm, the adhesion tension, A, of the binder (the product of the water-binder interfacial tension and cosine of the contact angle) may be expressed as follows:

$$A = 72\ p/P \text{ dyne/cm} \tag{1}$$

In the experiments, measurements were included of the aggregates after they have been treated thoroughly with NaCl and NaOH followed with rinsing with distilled water. In Table 6, the results are given for complete exchange. The results of measurements with stones treated with 0.05 N NaOH for 1 hr (200 g stone with 1 liter NaOH) followed by a thorough rinsing are also shown as partly exchanged. It is seen how the adhesion decreases with exchange with Na. NaCl is not as effective as NaOH. Riedel and Weber (23) have already ascertained the bitumen-displacing action of NaCl solutions. The reason must be found in the exchangeable Ca ions being replaced by Na ions, with reduced adhesive ability as a consequence. Nüssel and Buhs (26) have found that an emulsion

becomes more stable on addition of KCl. For the limestone which does not have ion-exchanging qualities, a treatment with NaCl or NaOH has little influence. This is in good agreement with the fact that the Øland limestone is the aggregate with the greatest blocking-up tendency against alkaline emulsions and with breaking numbers reduced least against emulsions where the NaOH surplus increased.

The conclusion must be that the breaking in a Weber and Bechler experiment is chiefly caused by the destruction of the emulsifier by formation of insoluble Ca and Mg soaps. The examined anion emulsions will convert the aggregates according to their greater or smaller ion exchange ability into aggregates with more or less diminished adhesion properties. At the same time, Ca ions are disengaged in an amount dependent on the pH of the emulsion, as well as on the ion exchange capacity, the content of calcium carbonate, and on the degree of the blocking-up of the stone surface by coagulated bitumen. These Ca ions will precipitate Ca soap both from the alkali metal soap which is present as an emulsifier film around the emulsion particles, and from the alkali metal soap which is found, principally in form of micelles, in the continuous phase. The coagulation which is measured will, therefore, be dependent on the amount of fatty acid anions, on the coagulating Ca ions available, and on the way these Ca ions distribute themselves between the fatty acid anions in the emulsifier film and in the micelles. This distribution is again dependent on the attraction between the stone and the asphalt bitumen that manifests itself in the measured adhesive ability which decreases with increasing content of KOH in the water phase.

The acid action of the stones or the adsorption of emulsifier (27), which earlier was thought to be the most important cause of the breaking, seems to be of less importance.

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