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# Evaluation of continuous shear and creep rheometry in the physical characterisation of ointments

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**Abstract**

Five commercial preparations are characterised physically using creep and continuous flow shear rheometry after they were classified as low or high stress-resistant by penetrometry and extensometry. Several rheological procedures are tested. The difference between the procedures is determined by the course of the stress as a function of time. Evaluation of the shear rheological method is performed by analysing the creep and flow curves and also the parameters calculated by using the mathematical Herschel–Bulkley curve-fitting model. Since the measuring results are dependent on the procedure applied, the scope of the measurement is an important criterium in selecting a procedure. 

*Keywords:* Continuous flow rheometry; Creep rheometry; Extensometry; Herschel–Bulkley analysis; Penetrometry; Semisolids

## 1. Introduction

The clarification of the microstructure of semisolids is an important issue in optimizing the formulation and manufacturing techniques of topical pharmaceutical dosage forms. Oil in water creams were investigated using different physicochemical techniques including small angle X-ray diffraction (Junginger et al., 1979; Junginger, 1984), differential scanning calorimetry (Junginger, 1984), thermogravimetry (Junginger, 1984; Junginger and Heering, 1984) and freeze fracture technique (Junginger, 1984; Patel et al., 1985), transmission electron microscopy (Junginger, 1984; Patel et al., 1985) and laser Raman spectroscopy (Louden et al., 1985). It was revealed that the creams consist of two different colloidal gel structures, both forming a coherent network. In the case of an O/W ointment the hydrophilic

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Table 1
Qualitative composition of the different ointments

| Ointment/component | Cremor Lanette I FNA | Basis Non-Ionicus | Cremor Cetylalcoholis | Beelerbasis | Coldcream |
|---|---|---|---|---|---|
| Emulsifying agent | Na-laurylsulphate | Cetomacrogol 1000 | Na-laurylsulphate | Na-laurylsulphate | Na-laurylsulphate |
| Oil phase | Cetylstearyl-alcohol | Cetylstearyl-alcohol | Cetylstearyl-alcohol | Cetylalcohol | Cetylalcohol |
| | Cetiol V | Cetiol V | — | White wax | Octyl gallate, almond oil, white wax |
| Aqueous phase | Sorbitol sol. 70% g/v, aqua pur. | Propyleenglycol, water | Glycerin, water | Propyleenglycol, water | Citric acid, propyleenglycol, water |
| Preservative | Sorbic acid | Sorbic acid | — | — | Butyl-hydroxy-anisol, *p*-hydroxybenzoate esters, sorbic acid |

gel phase is characterised by an interlamellar water layer, which is in a dynamic equilibrium with the bulk water phase. The second network consists of the lipophilic gel phase, which immobilizes the inner dispersed phase (Junginger, 1984; Junginger and Heering, 1984).

The most suitable characterisation of ointments and creams in order to evolve the gel network theory was achieved by using rheology. Both creep and continuous shear rheology are employed to determine viscosity, pseudoplasticity, yield values and thixotropy (Barry, 1983; Goggin et al., 1998). Since gels are visco-elastic materials, i.e. possess both liquid and solid characterisitics, also oscillatory rheology measurements are applied to determine the storage modulus $G'$ and loss modulus $G''$ (Barry, 1983; Goddard et al., 1991; Goggin et al., 1998).

The aim of the present study is to evaluate continuous flow and creep shear rheology in the physical characterisation of semisolids. The use of modern controlled-stress rheometers allows to change parameters, which were considered constant when using older rheometers. Hence, rheological procedures need to be formulated to examine the influence of the course of the applied shear stress as a function of time on the flow curves and on the parameters characterising the flow curves, such as thixotropy, pseudoplasticity and yield value. Since the recovery of a material after its deformation is strongly dependent on its stress-history, varying the measuring time interval during which the material is sheared, can influence the behaviour of the material. Further, the rheological technique, which applies shear stresses, is compared with two reference methods to measure consistency and spreadability, namely extensometry and penetrometry. Both reference techniques apply normal stresses.

## 2. Materials

The following ointments were obtained from Conforma (Destelbergen, Belgium): Beelerbasis NFVI (Formularium Nationale, 1988), Cremor Lanette I FNA (Formularium der Nederlandse Apothekers, 1985), Cremor Cetylalcoholis NFVI (Formularium Nationale, 1988), Coldcream CF, Basis Non-Ionicus NFVI (Formularium Nationale, 1988). The qualitative composition of the different ointments is given in Table 1. The emulsifying agent in all formulations is the anionic

Table 2
Characteristics of penetrating objects and matching containers

| | Macrocone | Microcone |
|---|---|---|
| Cone characteristics | | |
| Tip angle | 30° | 25° |
| Cone angle | 90° | 70° |
| Length | 47 mm | 9.8 mm |
| Largest diameter | 65 mm | 8.2 mm |
| Weight (cone and shaft) | 150.02 g | 23.78 g |
| Container characteristics | | |
| Diameter | 76.5 mm | 9.5 mm |
| Height | 63 mm | 57 mm |

Table 3
Rheometry procedures, creep procedures

| Creep procedure | Yield stress determination (YSD) |
|---|---|
| Temperature | 24°C |
| Applied stress | Increasing values |
| Step time | 10 min per value |

Na-laurylsulphate, except for Basis Non-Ionicus where the non-ionic Cetomacrogol 1000 is used. Cetylalcohol or cetylstearylalcohol is added to increase the consistency of the ointments. Water and oil phase differ in composition depending on the ointment considered.

## 3. Methods

### 3.1. Reference method 1: penetrometry

The definition of the measurement of consistency by penetrometry, according to the European Pharmacopoeia III is [… to measure, under determined and validated conditions, the penetration of an object into the product to be examined present in a container with specified shape and size.] (Pharmacopée Européene, 1997). The instrument used was an automatic microprocessor controlled penetrometer P734 (Analis, Namur, Belgium). As penetrating object two different double-tipped cones, further referred to as macro and microcone, were used. Their characteristics are summarised in Table 2.

Three methods to prepare samples for penetrometry are described in the monography. In examining ointments, Beck and Nürnberg compared the different methods and found method A the most reproducible (Beck and Nürnberg, 1996). Preliminary tests confirmed their findings. The ointment to be examined was brought into the appropiate container, depending on the cone used. The containers were filled carefully and completely, avoiding air bubble formation, and levelled with a spatula to obtain a flat surface. The small containers were filled using a syringe and levelled with a spatula. To obtain reproducible results, a rest period of 24 h at room temperature is necessary for the reconstruction of the ointment, which is disturbed during the transfer of the sample into the penetration containers. Instead of a one point measurement as described in the European Pharmacopoeia where the penetrating time for the object is 5 s, the penetration kinetics as a function of time were registered. The shaft and cone were released and allowed to penetrate into the sample for 30 min. The penetration depth, expressed in tenths of millimeters, was read from the display, every 5 s during the first minute, then every minute and from 10 min measurement time on, every 5 min. The mean penetration depth and standard deviation were calculated from three measurements. The correlation with the applied stress can be calculated, because stress is considered as a force exerted on a surface. The force is correlated with the weight of the cone, while the surface can be calculated from the penetration depth.

$$G = W \times g$$

Where $G$ is the force (N); $W$ is the weight of the cone (kg); and $g$ is the gravity constant (9.81 m $s^{-2}$). The surface area is calculated as the contact surface area between the cone and the sample (calculated from penetration depth). Stress is calculated as $G$ divided by the surface area.

As the force is constant because of a constant cone weight and the contact surface area is increasing with penetration depth, the stress decreases with time.

### 3.2. Reference method 2: extensometry

The spreadability of the ointments was measured with an extensometer as proposed by Pozo and Suñé (Del Pozo and Suñé, 1955). The apparatus consisted of a 140 mm diameter glass plate fixed in a holder and a second glass plate 95 mm in diameter with a mass of 33.88 g. Experiments were carried out at room temperature. The sample (0.500 g) was applied to the center of the largest glass plate and the second glass plate was put on the sample. After a 3 min equilibrium time, the diameter of the ointment spread between the two plates was measured.

Table 4
Continuous flow procedures

| Flow procedure | Logaritmic–equilibrium LOGEQ | Linear–equilibrium LINEQ | Linear–no equilibrium LINNONEQ |
|---|---|---|---|
| Temperature | 24°C | 24°C | 24°C |
| Controlled variable | Shear stress | Shear stress | Shear stress |
| Start value–>End value | Step 1: 1–>200 Pa | Step 1: 200–>1 Pa | Step 1: 1–>200 Pa |
| | Step 2: 200–>1 Pa | Step 2: 1–>200 Pa | Step 2: 200–>1 Pa |
| Ramp mode | Logarithmic | Linear | Linear |
| Number of points | 100 | 100 | 100 |
| Wait for equilibrium | Yes | Yes | No |
| % Tolerance | 1 | 1 | 1 |
| Max. point time | 15 s | 15 s | 15 s |
| Consecutive within | 5 | 5 | 5 |

Weights of increasing magnitude (20, 40, 60 and 80 g) were placed on the upper glass plate. After 3 min the diameter of the spread sample was measured again. Experiments were performed in triplicate and the mean diameter was calculated.

### 3.3. Shear rheometry

The rheological behaviour of the ointments was examined using a controlled stress rheometer Carri-med CSL2 100 (TA Instruments, Gent, Belgium), equipped with cone and plate configuration. To evaluate the influence of shear stress, shear rate and application time on the different materials used in this study, both continuous flow and creep procedures were proposed. The general principle of the former is a series of imposed consecutive changes in shear stress and the detection of the subsequent shear rates. The creep procedure deals with an imposed constant stress and the detection of the subsequent strain as a function of time. An overview of the different procedures is given in Tables 3 and 4. Experiments were performed in triplicate.

#### 3.3.1. Creep procedure

The creep procedure can be applied to characterise the visco-elastic behaviour of the ointments and to calculate the yield value. Therefore the different parts of the curve are analysed mathematically using the Voight model theory.

#### 3.3.2. Continuous flow procedure

The flow procedure can be divided into two steps. During the first step, the stress is increased from 1 to 200 Pa, during the second step the stress range is completed in the reversed order. The stress value of 200 Pa is the maximum stress that can be applied to the ointments without torque overload. The flow procedures (logaritmic equilibrium (LOGEQ); linear equilibrium (LINEQ); and linear no equilibrium (LINNONEQ)) differ in their ramp mode and equilibrium time. The course of the shear stress as a function of time for the different flow procedures is presented in Fig. 1.

During a logarithmic ramp mode, the majority of the measuring points is selected in the low stress region. Reaching a shear stress value of 100 Pa during a LOGEQ ramp mode takes 1650 s, almost 0.5 h. The maximum shear stress value of 200 Pa is reached after 1830 s, only 3 min later. The decrease of the shear stress shows the same tendency. The shear stress decreases rapidly in the beginning and more slowly as soon as the shear stress is low. During a linear ramp mode, the measuring points are equally divided over the whole range. In case of a LINEQ-procedure the shear stress value of 100 Pa is reached after just 930 s, 0.25 h. It takes another 9 min to attain the maximum value of 200 Pa. The decrease of the shear stress again shows the same tendency.

The flow procedures can also differ in their

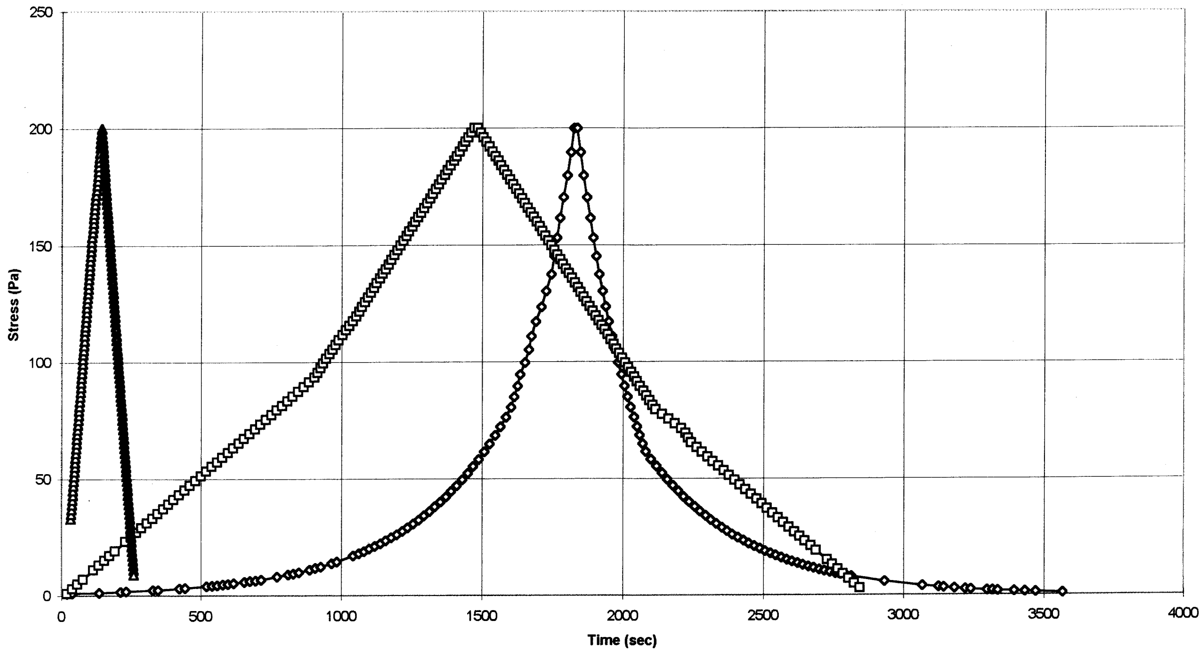



Fig. 1. Continuous flow procedures. Stress–time curve. LINNONEQ procedure (△), LINEQ-procedure (□), LOGEQ-procedure (◇).

equilibrium time. During an equilibrium procedure (LOGEQ-LINEQ), measuring points are subjected to an equilibrium criterium. The criterium covers the demand that the results of five consecutive measurements at the same stress differ 1% at the most. The instrument will continue to measure at the same stress until the measuring results comply with this demand, unless the time required to reach equilibrium exceeds 15 s. An equilibrium measurement always takes more time in comparison to a non-equilibrium measurement (50–60 min vs 5 min).

The curves were analysed with the data analysis software, using different mathematical models. The best curve fitting model seemed to be the Herschel–Bulkley model (Eq. (1)). This model can be compared to the Power Law model, except for the fact that Herschel–Bulkley takes the yield stress into account. Yield stress, consistency, pseudoplasticity and thixotropy can be calculted using this mathematical model.

$$\tau = \tau_y + KD^n \quad (1)$$

Where $\tau$ is the shear stress; $\tau_y$ is the yield stress; $K$ the Herschel–Bulkley viscosity coefficient; $D$ the shear rate; and $n$ the rate index (pseudoplastic material: $n < 1$).

Yield stress can also be calculated without a mathematical model. The yield stress is the critical stress that needs to be exceeded before any flow is detected. Hence, the yield stress can be derived from the continuous flow data, choosing the shear stress below which no significant shear rate is detected.

## 4. Results and discussion

### 4.1. Penetrometry

Results obtained from the penetrometer are expressed as the average penetration depth as a function of time. The maximum standard deviations of the penetration depths for macro and microcone are 1 and 10%, respectively. Penetration stress as a function of time is given in Figs. 2 and 3 for the macro and the microcone, respectively.

The first characterising parameter is the magni-

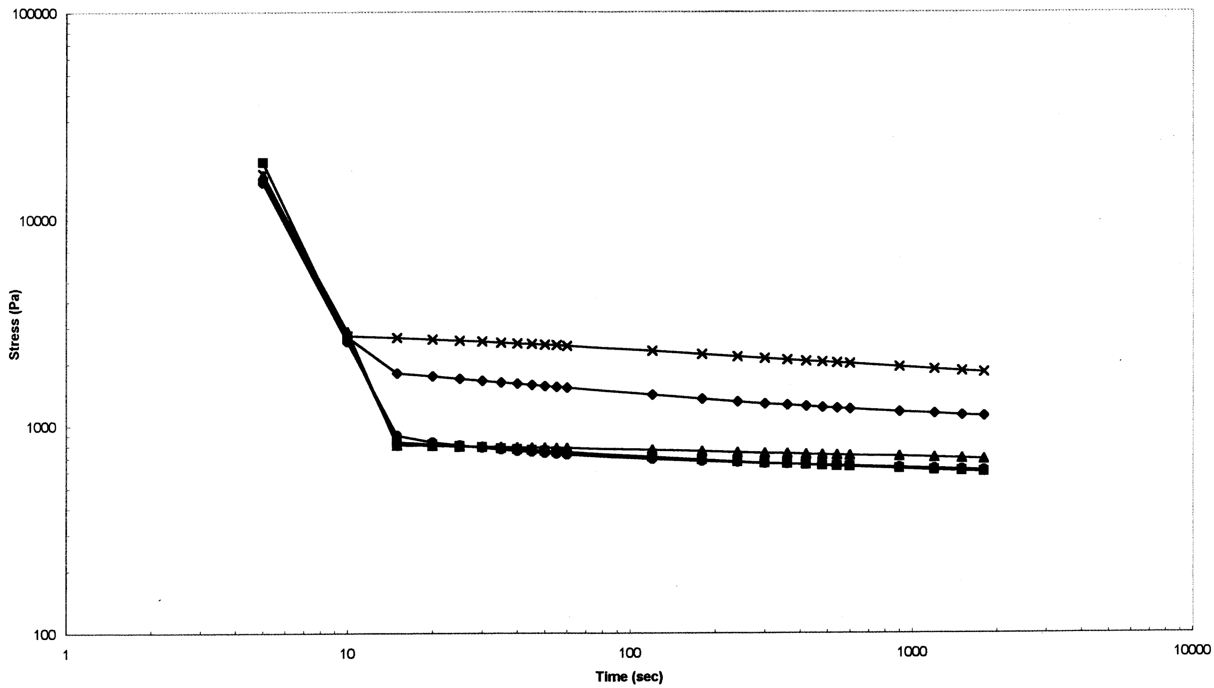



Fig. 2. Penetration kinetics–macro-cone. Ointments: Cremor Lanette (◆), Basis Non-Ionicus (●), Cremor Cetylalcoholis (▲), Beeler Basis (■), Coldcream ( × ).

tude of stress. Considering this parameter, the ointments can be divided into two groups independent of the geometry of the cones: the high stress-resistant (Coldcream, Cremor Lanette) and the low stress-resistant (Beelerbasis, Cremor Cetylalcoholis, Basis Non-Ionicus) ointments.

A second parameter is the slope of the penetration curve. For the macrocone, the curve is divided into two parts. Initially a deep penetration and a fast stress fall is recorded. After this stress fall, the slope of the penetration stress curve becomes very low. During this second part, the slopes for the different ointments are comparable. Penetration reached almost its maximum value and a near-equilibrium stress was attained.

The curves obtained with the microcone consist of only one part. There is a marked difference between Cremor Cetylalcoholis, Basis Non-Ionicus and Beelerbasis on the one hand and Cremor Lanette and Coldcream on the other hand. The former group is the low stress-resistant one, allowing deeper penetration and lower stresses. The latter is the high stress-resistant group, only a low penetration occurs. Because of its lower weight, the microcone is only capable of penetrating low stress-resistant ointments and this is characterised by a slow penetration velocity. The microcone penetrates hardly into high stress-resistant ointments.

### 4.2. Extensometry

The extensometry results comprise the diameters of the spreaded samples as a function of the weight applied or time. The second glass plate exerts a normal stress on the material. Whereas in penetrometry the force is constant and the contact surface area increases, both force (increasing weight) and surface area (increasing diameter) are extended in extensometry. The measurements on the samples result in a force increasing more in relation to the spreading surface area, so the final result is an increasing stress. Calculating the stress from the force/surface area ( $\propto$ weight/diameter) relation, results can be graphically represented as

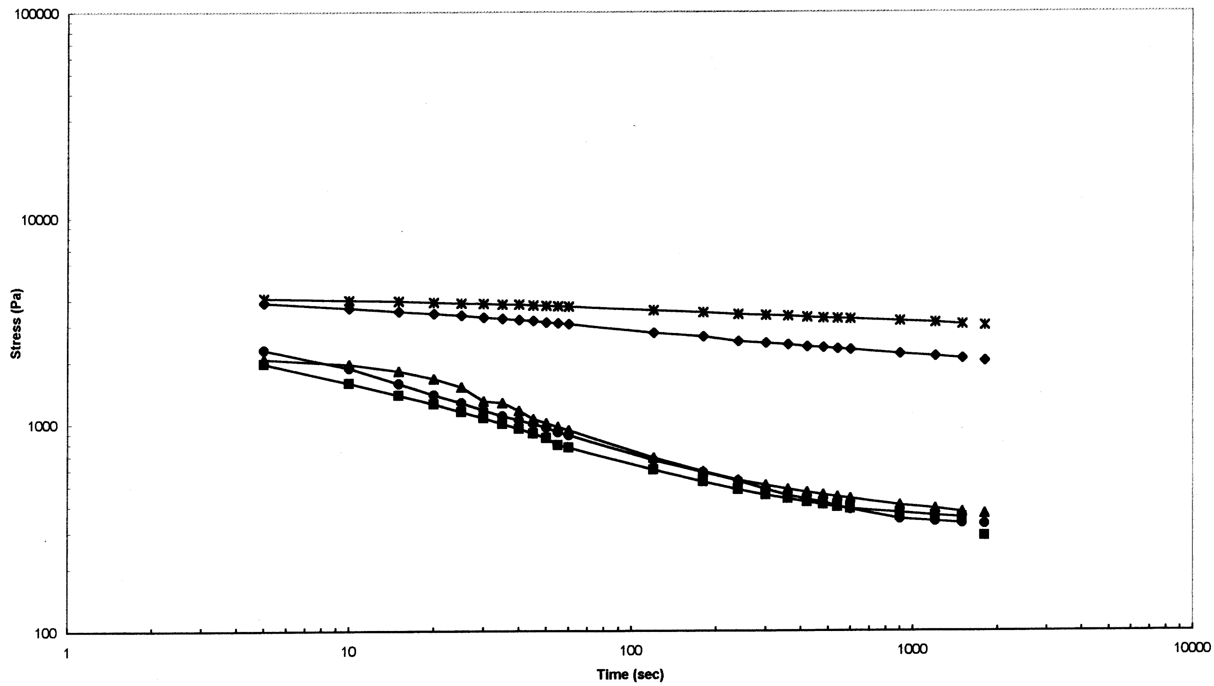



Fig. 3. Penetration kinetics–micro-cone. Ointments: Cremor Lanette (◆), Basis Non-Ionicus (●), Cremor Cetylalcoholis (▲), Beeler Basis (■), Coldcream ( × ).

a plot of stress versus time. This plot is shown in Fig. 4, which indicates that the general tendency of the penetrometric measurements is also seen when applying extensometry. Coldcream and Cremor Lanette exhibit the most spreading-resistant behaviour. The extensometric stress remains high and increases with time, because the increasing weight only makes the high stress-resistant ointments spread minimally. Spreading-allowing ointments like Cremor Cetylalcohol and Beelerbasis will spread more and faster when subjected to an increasing weight. The similarity between Basis Non-Ionicus, Cremor Cetylalcoholis and Beelerbasis found in penetrometry is not observed in extensometry. Basis Non-Ionicus shows a more spreading-resistant like behaviour (Coldcream, Cremor Lanette) than spreading-allowing behaviour (Cremor Cetylalcoholis, Beelerbasis).

### 4.3. Shear rheometry

#### 4.3.1. Creep measurements

Fig. 5 illustrates the retardation curve at a shear stress of 15 Pa and the recovery curve (0 Pa) of Beelerbasis. The retardation curve can be divided into three parts. The first part is the instantaneous compliance (hardly present in Beelerbasis), representing the instantaneous elastic component of the material. The visco-elastic nature of the material is represented by the second part and characterised by one or more Voigt units. The last part of the curve, during which strain is increasing linearly with time, characterises the zero shear viscosity of the material. Computer software allows to calculate the elastic and viscous component as well as the visco-elastic component of the material. In Fig. 6 the retardation curve at a shear stress of 17 Pa and the recovery curve (0 Pa) are shown. The shear stress is high enough to break down the bindings responsible for the elastic behaviour. The strain increases enormously and the behaviour of the material is purely viscous. The absence of elastic components allows the material to flow freely, that is the yield value is exceeded and the shear rate starts to increase.

The Voigt analysis results indicate that a pure

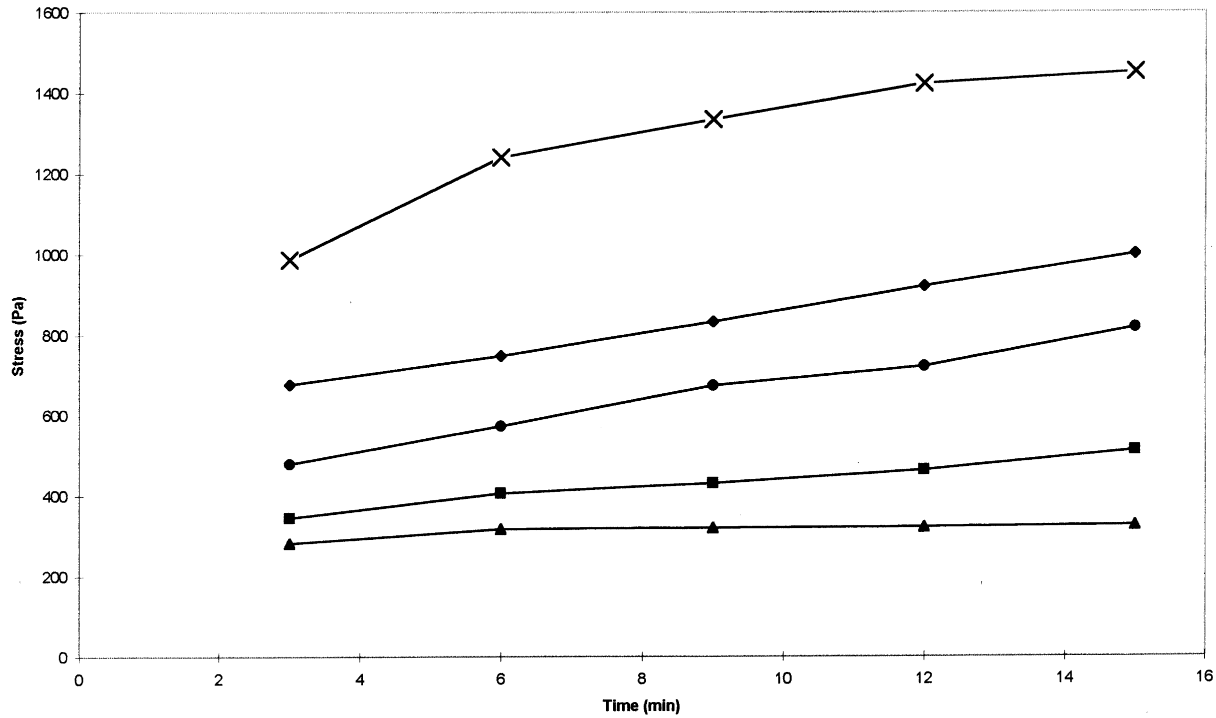



Fig. 4. Extensometry. Stress–time plot. Ointments: Cremor Lanette (◆), Basis Non-Ionicus (●), Cremor Cetylalcoholis (▲), Basis Beeler (■), Coldcream ( × ).

elastic response is hardly detected in the ointments studied. However, there are two visco-elastic Voight units present in each ointment. Coldcream is characterised by three Voigt units. In Table 5, two other parameters calculated using the creep data, are presented: (1) the yield stress; and (2) the newtonian viscosity at a shear stress value just below the yield stress. Coldcream is the only ointment having a high yield stress. The yield stresses of the other ointments are comparable, Cremor Lanette having the lowest and Cremor Cetylalcoholis having the highest yield stress. The newtonian viscosity is the highest for Coldcream and the lowest for Cremor Cetylalcoholis. Beelerbasis, Cremor Lanette and Basis Non-Ionicus have comparable newtonian viscosities.

*4.3.2. Continuous flow measurements*

The flow curves of the different ointments, obtained with LOGEQ and LINNONEQ procedures are shown in Figs. 7 and 8. Considering the shear rates as a function of shear stress, it can be concluded that independently of the procedure applied the resistancy of the different ointments against a stress, as determined using the penetrometric and the extensometric method, is roughly maintained.

The LOGEQ-procedure allows to make a clear distinction between the ointments. The ranking order of the shear rate magnitude (inversely proportionate to the stress-resistancy) is Basis Non-Ionicus > Beelerbasis > Cremor Cetylalcoholis > Cremor Lanette > Coldcream. On the other hand, the use of the LINNONEQ procedure allows us to make the same distinction, but not as clear as with the LOGEQ procedure. The same ranking order is obtained for the different ointments at 200 Pa. However, when comparing the shear rates at 150 Pa the ranking order is difficult to establish and is above all different from that obtained with the LOGEQ

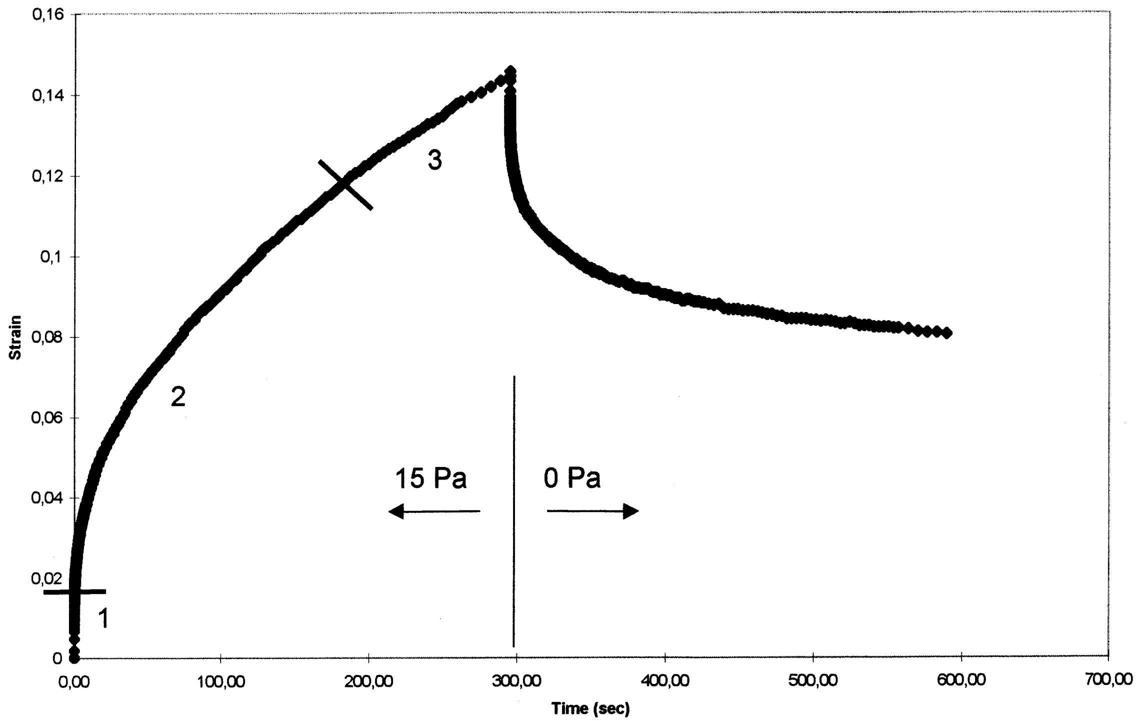



Fig. 5. Creep procedure. Retardation–recovery curve of Beelerbasis (15–0 Pa).

procedure. Composing a complete flow diagram using the LINEQ procedure was not possible. Often the angular velocity exceeded the maximum value tolerated by the rheometer, because of complete structure breakdown. This resulted in an automatic ending of the LINEQ measurement.

The data obtained using the different procedures indicate that defining the parameters when setting up a continuous flow procedure is very important. The former example demonstrates that in case of the ointments selected, using the LOGEQ procedure is recommended. This choice is justified when the stress–time curves in Fig. 1 are considered. When applying a LINEQ procedure the sample is subjected to large shear stresses from the beginning of the measurement on because the shear stress increases linearly with time. This often results in complete breakdown of the structure. On the contrary, when using a LOGEQ procedure, the time span during which the sample is submitted to high stresses is much shorter. In a LINNONEQ-procedure shear stress also increases linearly with time, but since the equilibrium demand is not built in the procedure, the time span during which the stresses are imposed on the sample is shorter. Structure breakdown does not occur. However, the shorter measuring time is responsible for a smaller difference between the flow diagrams of the different ointments.

When the flow diagrams obtained with the continuous flow procedures are compared to the penetrometric and extensometric results, it is clearly demonstrated that the LOGEQ diagrams are in best accordance with the results of the reference methods. Since this comparison only concerns the shear rate ranking order of the flow curves, further analysis of the flow data is necessary using the mathematical Herschel–Bulkley model.

Figs. 9 and 10 present the regression coefficients and the standard deviations, obtained when applying the Herschel–Bulkley model to the flowcurves of the ointments. The standard devia-

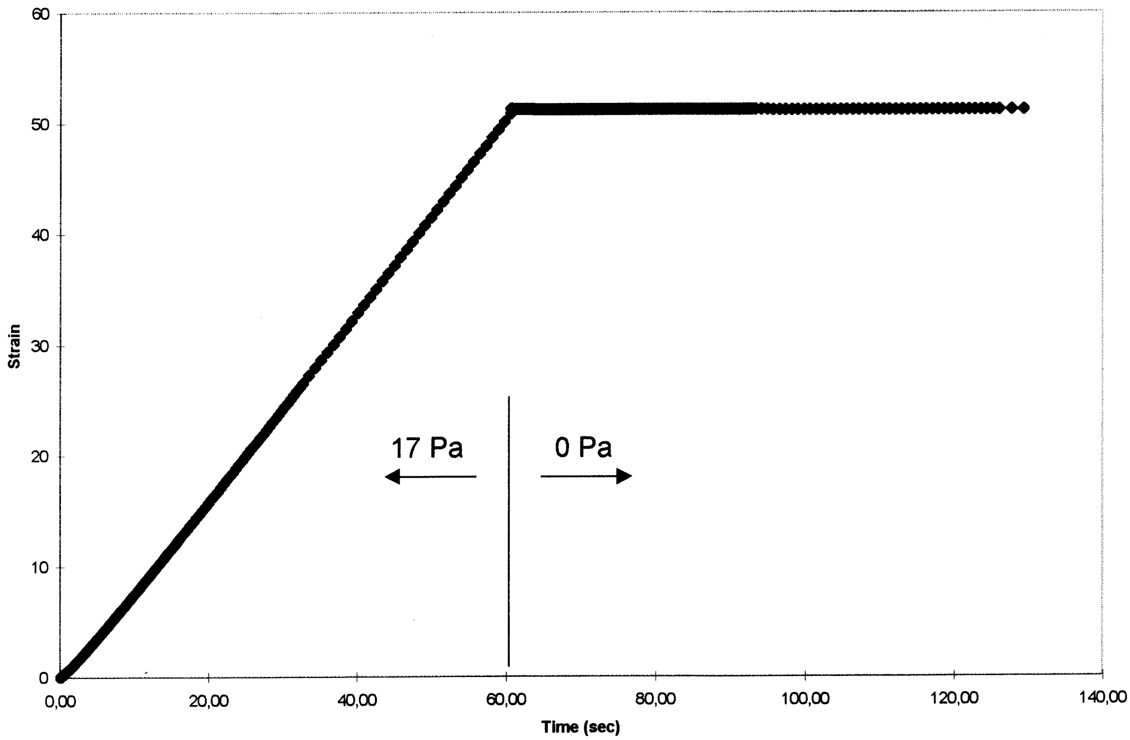



Fig. 6. Creep procedure. Retardation–recovery curve of Beelerbasis (17–0 Pa).

tion is a measure for the accuracy of the curve-fitting proces. For all ointments the standard deviation is the lowest when applying the Herschel–Bulkey model. When applying other models (Casson, Power Law, Bingham, Newtonian) standard deviations are larger and the curve-fitting process is less accurate. This indicates that all ointments show non-newtonian flow and have a yield stress. Only in the case of Basis Non-Ionicus the standard deviations for Herschel–Bulkley and Power Law are the same, indicating the absence of a yield stress. The differences between the standard deviations of LOGEQ and LINNONEQ flow curves are minimal, although there is a tendency for higher standard deviations in the case of the LOGEQ procedure, except for Beelerbasis. The high standard deviation for the Coldcream LOGEQ flow curve can be explained by a poor curve fitting, even by the Herschel–Bulkley model.

Table 5
Creep results, yield stress and newtonian viscosity

| Ointment | Yield stress (Pa) | Newtonian viscosity (Pas) |
|---|---|---|
| Beelerbasis NFVI | 19 | 215 400 |
| Cremor Cetylalcoholis NFVI | 27 | 47 600 |
| Coldcream CF | 121 | 1438 000 |
| Cremor Lanette I FNA | 17 | 218 700 |
| Basis Non-Ionicus NFVI | 21 | 316 100 |

The regression coefficients are higher when applying a LINNONEQ procedure. Since the measuring points are divided linearly over the whole measuring range, the calculation of the regression coefficient is more accurate, compared to the LOGEQ procedure.

The Herschel–Bulkley viscosity coefficient $K$

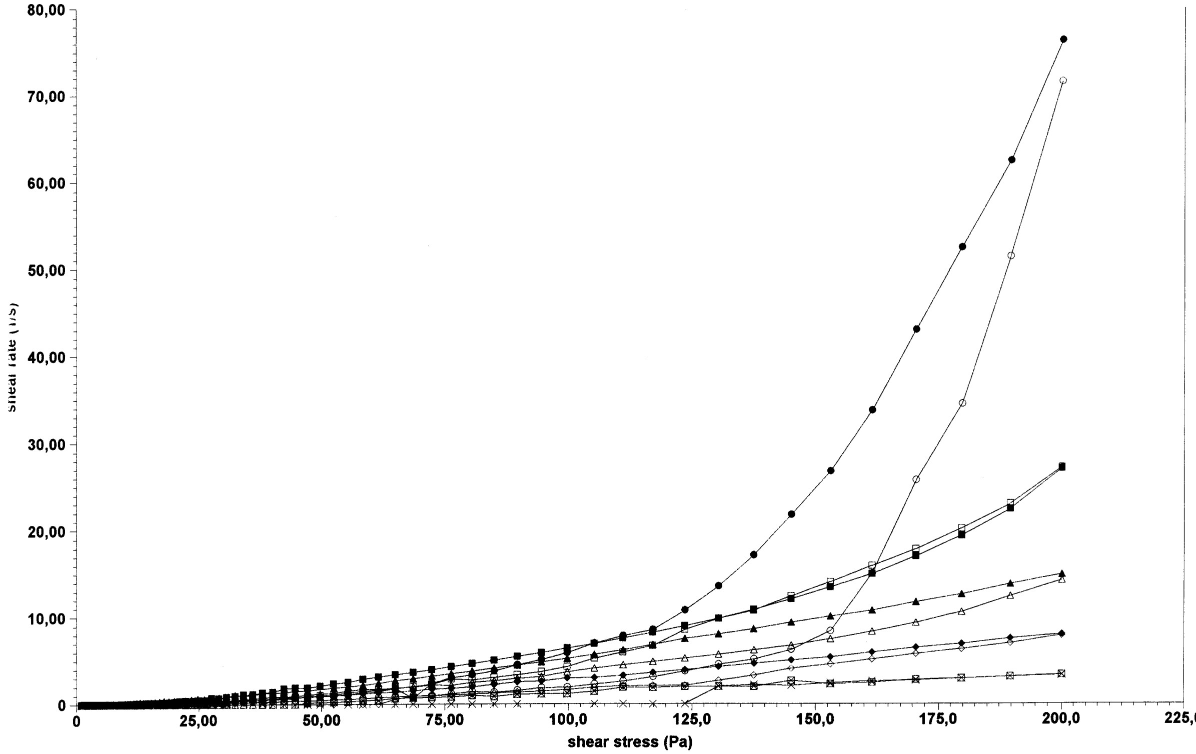



Fig. 7. Flow curves LOGEQ procedure. Flow step 1 = 1− > 200 Pa (filled symbols); flow step 2 = 200− > 1 Pa (open symbols). Ointments: Cremor Lanette (◇, ◆), Basis Non-Ionicus (○, ●), Cremor Cetylalcoholis (△, ▲), Basis Beeler (□, ■), Coldcream (×, ×).

and the rate index $n$ are presented in Figs. 11 and 12. In case of the low stress-resistant ointments (Beelerbasis, Cremor Cetylalcoholis and Basis Non-Ionicus) the Herschel–Bulkley viscosity coefficients, obtained with the LINNONEQ-procedure, are higher compared to the coefficients obtained with the LOGEQ procedure. Although the shear stress increases linearly with time during a LINNONEQ procedure, the viscosity coefficients are higher. This can be explained by the absence of an equilibrium time, essential during a LOGEQ procedure. For the high-stress resistant Cremor Lanette, there is no significant difference between the viscosity coefficients. Comparing the viscosity coefficients of Coldcream is almost impossible because of poor curve-fitting.

The rate index $n$ of the ointments is smaller than 1, indicating a pseudoplastic behaviour. The differences between the indices, calcuted using the LOGEQ and LINNONEQ flow diagrams, are rather small. To make comparisons is not recommended because the standard deviations are larger than the differences between the indices.

In Fig. 13 the thixotropic level for the different procedures applied on the ointments is presented. In the case of Beelerbasis and Cremor Cetylalcoholis the level of thixotropy increases when using the LINNONEQ procedure. Little difference in thixotropy is seen when comparing both procedures for the high stress-resistant ointments Coldcream and Cremor Lanette. Basis Non-Ionicus is more thixotropic when subjected to a LOGEQ-procedure.

The degree of thixotropy seems to be independent of the procedure applied in the case of more stress-resistant ointments. If the stress-resistance is lower, the level of thixotropy increases using the LINNONEQ procedure, as observed for Beelerbasis and Cremor Cetylalcoholis. Although a

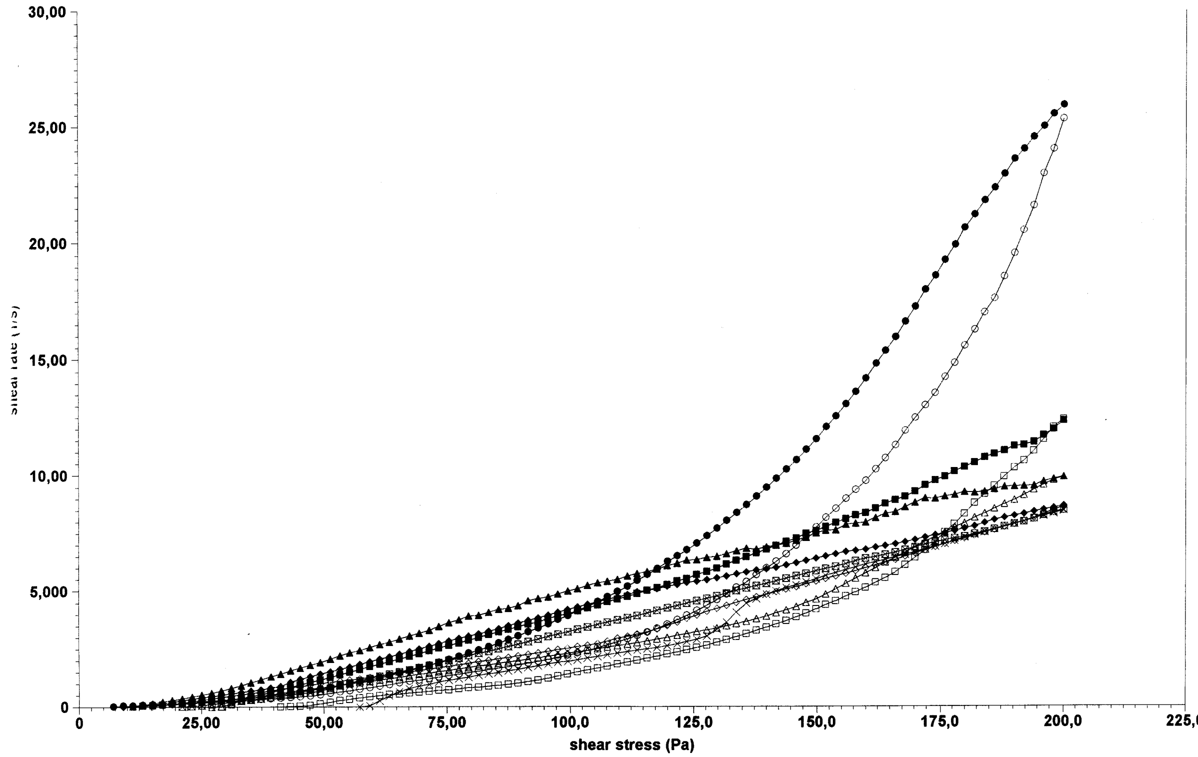



Fig. 8. Flow curves LINNONEQ procedure. Flow step 1 = 1– > 200 Pa (filled symbols); flow step 2 = 200– > 1 Pa (open symbols). Ointments: Cremor Lanette (◇, ◆), Basis Non-Ionicus (○, ●), Cremor Cetylalcoholis (△, ▲), Basis Beeler (□, ■), Coldcream (×, ×).

LINNONEQ measurement is rather short, the high stress values come after each other very fast. In case of a LINNONEQ procedure, more than half of the 100 measuring points are above 100 Pa; in a LOGEQ procedure only 14 measuring points are above 100 Pa (Fig. 1). Although the measuring points at higher stresses are not subjected to an equilibrium demand, the molecules lose their former orientation resulting in a higher degree of thixotropy.

Basis Non-Ionicus seems not obey this rule. However, since this ointment is very low stress-resistant, the thixotropic level is high and the variation between the measurements considered is very large. To make a comparison between both procedures is questionable in the case of Basis Non-Ionicus because of the low repeatability and high standard deviations. Due to the low-stress resistancy, the structure of the ointment is somewhat broken down during the measurement, resulting in high standard deviations.

The curve-fitting is not accurate enough to calculate the yield values of the ointments considered using the Herschel–Bulkley model.

Another method to determine the yield stress is to consider the shear stress in the flow curve that causes a 1000-fold increase of the shear rate. Results are presented in Fig. 14. The yield values obtained from the LOGEQ-procedure are more or less in accordance with the data calculated using the creep procedure, Coldcream having the highest yield stress (138 Pa) and the other ointments situated in the lower yield stress region, between 20 and 50 Pa. When the LINNONEQ-procedure is applied, the yield stresses are much lower. The linear increase in the shear stress values during a LINNONEQ-procedure causes the breakdown of the bindings responsible for the

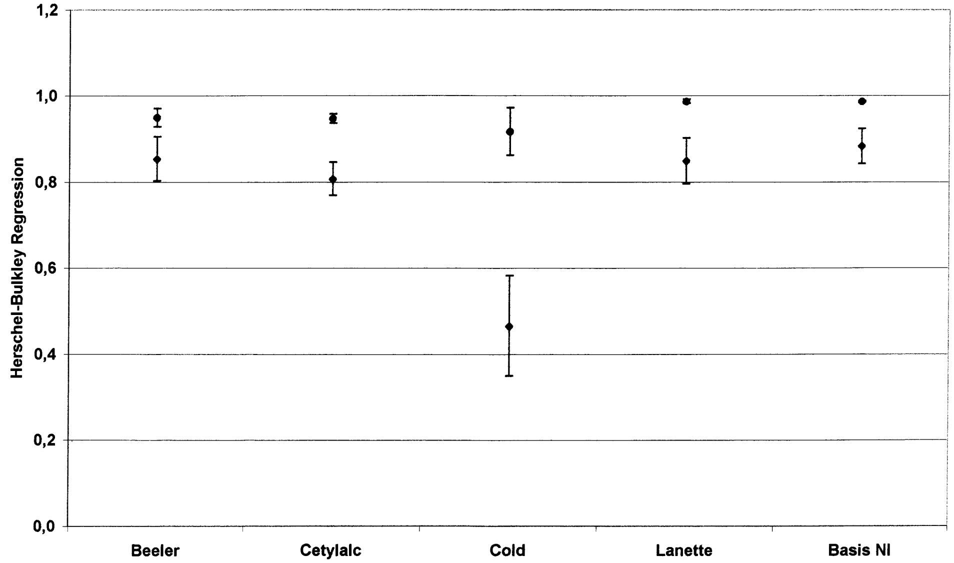



Fig. 9. Herschel–Bulkley analysis. Regression. Logeq-procedure (◆), Linnoneq-procedure (●).

viscoelastic behaviour of the material at lower shear stresses. During a LOGEQ procedure shear stress is increased more moderately and the viscoelastic bindings break at higher stresses.

## 5. Conclusions

Penetrometry as well as as extensometry are good reference methods that allow to divide the

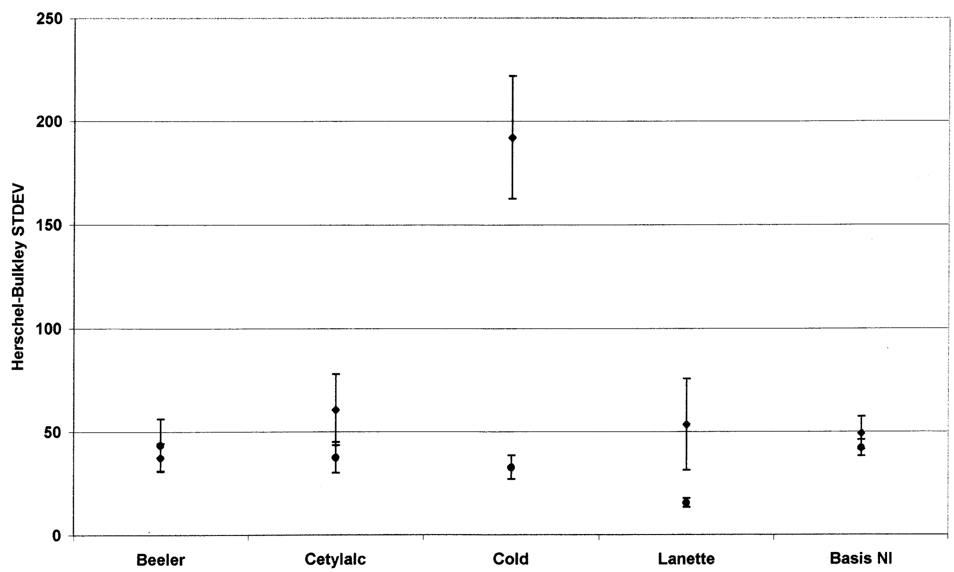



Fig. 10. Herschel–Bulkley analysis. Standard deviation. Logeq-procedure (◆), Linnoneq-procedure (●).

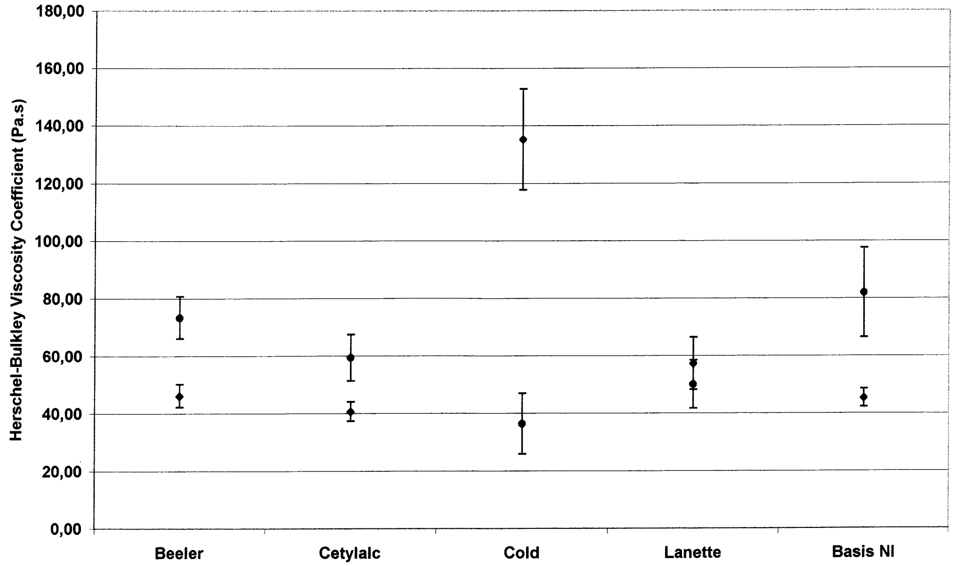



Fig. 11. Herschel–Bulkley analysis. Viscosity coefficient. Logeq-procedure (◆), Linnoneq-procedure (●).

ointments in low and high stress-resistant formulations. However, by using shear rheometry it is possible to investigate additional parameters characterising more profoundly the ointments studied. The creep procedure can be applied to determine the yield value and gives information on the viscoelastic behaviour of the material. The LINEQ measuring procedure is not useful. The shear stress is too large and breaks down the structure of the cream. The results of the LOGEQ continuous flow procedure are in accordance with penetrometric and extensometric results and the LOGEQ yield values can be compared with the yield values calculated using the creep procedure.

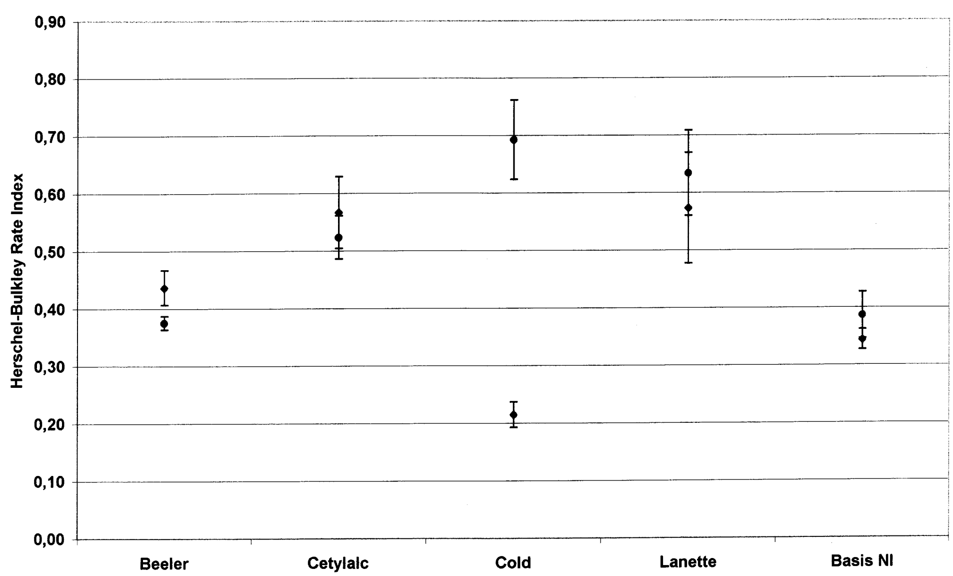



Fig. 12. Herschel–Bulkley analysis. Rate index. Logeq-procedure (◆), Linnoneq-procedure (●).

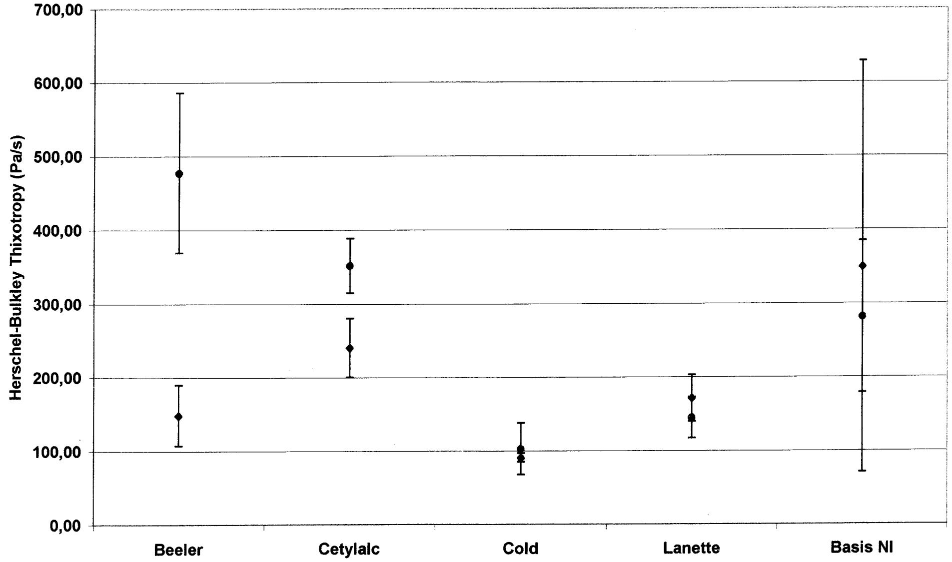
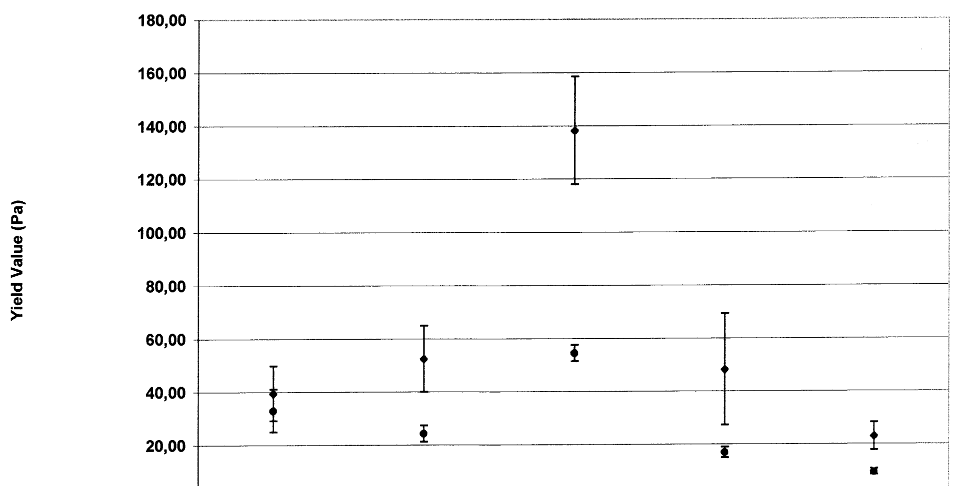



Fig. 13. Herschel–Bulkley analysis. Thixotropy. Logeq-procedure (◆), Linnoneq-procedure (●).

An alternative for the time-consuming LOGEQ procedure is the LINNONEQ procedure. LINNONEQ measurements are shorter because of the absence of an equilibrium demand. Although the influence on the viscosity coefficients, the rate index and the standard deviation of the curve-fitting process can be considered as minor, the quality of the flow diagrams of the LINNONEQ measurements is unsatisfactory to make a clear distinction between the different ointments. The yield values are lower and the thixotropic level of the low stress-resistant ointments is higher.




| | Beeler | Cetyl | Cold | Lanette | Basis NI |
|---|---|---|---|---|---|
| ◆ <Yield LOGEQ> | 39,67 | 52,54 | 138,43 | 48,39 | 23,13 |
| ● <Yield LINNONEQ> | 33,16 | 24,45 | 54,60 | 17,08 | 9,71 |

Fig. 14. Yield value. Continuous flow procedures.

Which measuring procedure to select can dependent on the scope of the measurements. However it should be taken into account that the procedure applied influences the measuring results.

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