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Research paper

Shear Flow of Guncotton Pulp

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Abstract: This article considers aspects of the flow, rheology, and viscometry of guncotton pulp. It is substantiated that during production guncotton pulp is subjected to shear deformation, taking into account sliding over smooth surfaces, in the input zones of the dies, in the barrel, and on the crimped finned tube of the screw extruder. At the same time, the presence of shear stress in guncotton pulp has not been established. A rotational viscometer with a torque meter, which was developed during this research, enabled the presence of shear stress in guncotton pulp to be demonstrated. The values of the flow stress depend on the solvent content in the guncotton pulp; as this is decreased, the τ_0 value increases. When the flow curve for the section from τ_0 to τ_{Rmax} was constructed, the flow curves of the guncotton pulp were described by the Herschel-Bulkley equation. The flow curves of guncotton pulp obtained on corrugated capillaries of different sizes are non-invariant and depend on the magnitude of the deformation of the guncotton pulp in the capillaries. Guncotton pulp flows in a narrow range of pressures and deformations.

Keywords: guncotton pulp, viscometry, shear flow, shear stress, torque

1 Introduction

Single-base smokeless powders have been produced worldwide for more than a hundred years, but the rheological properties of guncotton pulp (GP), from which the propellant is formed, have not been sufficiently studied. In the literature on gunpowder production, guncotton pulp is referred to as a power-law fluid

that flows in a narrow range of stresses [1]. It is noted that GP flows on smooth surfaces in a sliding mode [1, 2].

Interest in the rheological properties of GP arose in the USSR when complex equipment for the continuous production of single-base smokeless powder was created. The developers were faced with unstable operation of the screw extruders, which consisted of periodic cutting of the GP from the reefs of the extruder body and the termination of the work. Note that, in this context, “reef” is a longitudinal groove on the inner surface of the extruder body, designed to prevent the extruded medium from rotating with the screw. The reefs are structurally located on the entire inner surface of the extruder body. This feature of GP extrusion has led to the fact that only certain grades of large single-base smokeless powder grains can be produced using continuous production technology. Batches of small single-base smokeless powder grains are pressed on hydraulic presses, where the labour intensity of their production is several times higher than that of a continuous production process.

It has been noted in references [1, 3] that the study of the rheological properties of GP is associated with significant methodological difficulties. GP is a mixture of guncotton No. 1 and guncotton No. 2 with an alcohol-ether solvent. Guncotton No. 1 is a nitrocellulose with nitrogen content ~13.0-13.5%. Guncotton No. 2 is a nitrocellulose with nitrogen content ~12.2-12.4%. Guncotton No. 2 dissolves well in an ethereal solvent and its solution serves as a binder in the GP, while guncotton No. 1 essentially does not dissolve in an ethereal solvent and serves as an energetic filler. The average ratio of guncotton No. 1 to guncotton No. 2 in GP is ≈ 3 , and depends on the required energy of the powder. That is, GP is a highly filled medium, where the filler content in the finished powder can reach 75% and more. More than 75% of the filler can arise when the nitrogen content in the guncotton is less than 12%, then in order to provide the energy required in the finished gunpowder, guncotton No. 2 with an increased nitrogen content of 12.5-12.6% is introduced into the GP. The solubility of guncotton No. 2 with such a nitrogen content is reduced, and the GP becomes “tougher” and its extrusion becomes more difficult.

Nitrocellulose is a nitration product of plant cellulose. The particle shape of nitrocellulose in GP is a shredded cellulose fiber that is longer than its diameter. During the shear flow of GP, nitrocellulose fibers are oriented in the direction of shear, creating a powder structure. This strongly affects the rheological characteristics of GP [4, 5]. The presence of an alcohol-ether solvent in the composition of the GP also complicates a study of the properties of GP. Since the solvent is volatile and flammable, all viscometer equipment must be hermetically sealed and safe to handle [6].

All of these factors have led to the conclusion that the classification of GP as a rheological medium has not yet been established. The narrow range of GP flow, both in stress and in strain rates, is explained by the instability of the properties of nitrocellulose and the volatility of the solvent. GP is a plastic medium, but its flow stress has not been established. It is also impossible to explain with a power-law the fluid sections of the GP from the reefs.

The present article presents an investigation of the shear flow of GP using capillary and rotational viscometric methods, taking into account the peculiarities of GP and its handling. The purpose of the article is to qualitatively identify the type of tested GP as a rheological medium, as well as to clarify the features of the GP flow in the barrel of an extruder screw, as these data are crucial in the manufacturing process of single-base smokeless powders.

2 Materials and Test Method

Tested batches of guncottons No. 1 and No. 2 were standard powder masses of the Shostka powder factory (Ukraine). The content of the alcohol-ether solvent was 80%. The nitrogen content and solvent alcohol-ether ratios are listed in Table 1. From the literature, it is known that the alcohol-ether solvent ratio is usually 1:2. Samples with different ratios were tested because the aim was to determine the dynamics of change with respect to the well-known data for this commonly used ratio. The differences in the parameters specified in Table 1, *e.g.* for nitrocellulose with a nitrogen content of 13.4%, these indicate the variability of the properties of the raw materials.

In the production of a single-base smokeless powder, GP undergoes shear deformation, taking into account its sliding on smooth surfaces, in the inlet zones of the dies, in the barrel, and on the crimped finned tube of the screw extruder. When mixing, the GP undergoes shear deformation in the gaps between the blades of the screw and the barrel, but in appearance the GP after mixing is a free-flowing medium. The final dense structure of a single-base smokeless powder is formed in dies. The approximate effective viscosity of such a GP is from $30 \cdot 10^3$ to $40 \cdot 10^3$ Pa·s. While there are no fundamental technical difficulties for the study of the rheological properties by capillary viscometric methods, no one has yet succeeded in investigating the rheological properties of industrial GPs using rotational viscometric methods due to technical and methodological difficulties.

A technique for eliminating sliding of the test medium relative to the measuring surfaces when determining its rheological characteristics is the corrugation of these surfaces [7]. Therefore, in this research, corrugated surfaces were used

both in the capillaries and on the measuring surfaces of the rotary viscometer. Both the capillary and rotational viscometers were redesigned to reflect the properties of the GP.

The capillary viscometer was constructed based on the «UMM-5» tensile testing machine equipped with a gear box (Figure 1). A feature of this tensile testing machine is that the developed effort is balanced by the deflection of the pendulum (position 6). Its value was indicated on the force indicator (position 8).

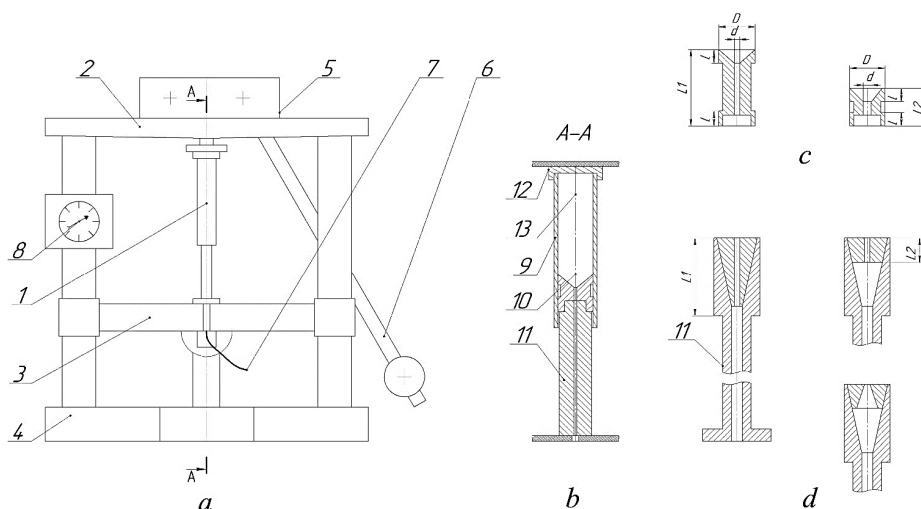


Figure 1. Capillary viscometer: (a) general view of the viscometer: 1 – viscometer device, 2 – fixed traverse, 3 – movable traverse, 4 – drive with gearbox, 5 – force-measuring device, 6 – pendulum, 7 – GP cord, 8 – force indicator, (b) general view of the viscometer unit with a moving capillary: 9 – mould, 10 – capillary, 11 – support, 12 – cover, 13 – investigated GP, (c) design of smooth capillaries, and (d) design of corrugated capillaries

The viscometer device (Figure 2) was redesigned and differed in that the capillaries in it were mobile. The need for such modification was that with a high viscosity GP, the resistance of the mass layer above the capillary when pushing it from above was commensurate with the resistance in the capillary itself. In other words, the resistance in the capillary decreased with decreasing height of the layer itself, and it was impossible to achieve a constant outflow pressure.

When the capillary moved from below into the pulp layer, the outflow pressure did not depend on the layer height, and its value was constant. Since the measurement was carried out according to the Bagley method, the lateral surface on

both long and short capillaries (position 2) was the same. This technique equalized the frictional losses during the movement of the capillaries. For the study of the shear flow of the GP, collapsible conical capillaries of different lengths were used, which were inserted into the support (position 3). The corrugations on the surface of the capillaries were a metric thread with an inner diameter of $6.65 \cdot 10^{-3}$ m. The capillary of zero length was a hole $6.65 \cdot 10^{-3}$ m in diameter with a sharp edge.

The rotational viscometer for studying the rheological properties of the GP had to be re-developed. In this redesign it was necessary to take into account the following features of the GP:

- Flammability (the flashpoint is 40-60 °C).
- Content of extremely volatile solvent (diethyl ether).
- The range of investigation of the pressure properties should cover a range of pressures up to ~15 MPa.
- Structural transformations in GP during shear can be accompanied by a decrease in shear resistance.
- High values of the effective viscosity of the GP will entail significant torque values for the drive of the viscometer, and the presence of special equipment for placing (pressing) the GP into the measuring gaps.

Such a rotational viscometer was developed based on a precision lathe, with the introduction of an additional gearbox into the kinematic chain of the machine. The measuring device of the viscometer was made according to the «coaxial cylinders» scheme, as the most appropriate for filling the GP into the measuring gaps (Figure 2).

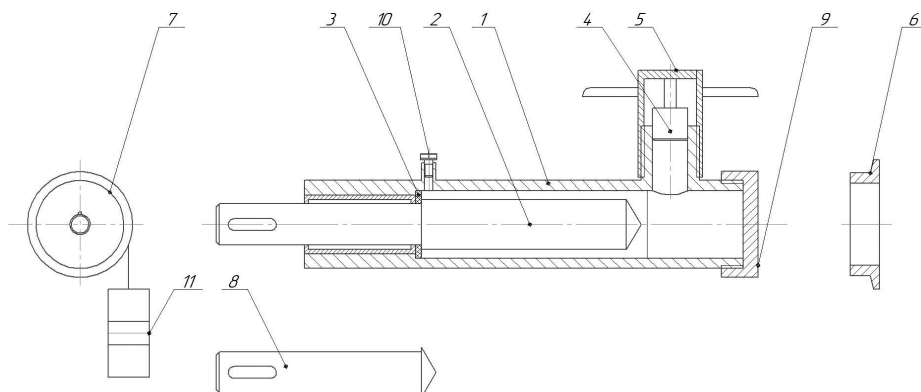


Figure 2. Scheme of a rotary viscometer for investigating the properties of GP: 1 – barrel, 2 – rotor, 3 – mechanical seal, 4 – plunger, 5, 9, 10 – plugs, 6 – adapter, 7 – calibration disc, 8 – rotor of zero length, 11 – set of weights

Additionally, a mixer-press was developed and manufactured for filling the viscometer with GP. The filling itself was carried out as follows: the plug (position 9) was replaced by an adapter (position 6), the plug (position 10) was removed, and the plunger (position 4) was also removed. In this form, the viscometer was connected to a mixer-press and filled with GP. After the GP cord emerged from the control hole under the plug (position 10), filling was stopped, the viscometer was disconnected from the mixer-press, the adapter (position 6) was replaced with a plug (position 9), and the viscometer was assembled with a drive through the torque meter (TM). The plug (position 5) was then disconnected, the plunger (position 4) was installed and the plunger (position 4) was pressed with a manual hydraulic press until the cord emerged from the hole under the plug (position 10). In this manner, a reliable filling of the measuring gap between the cylinders was ensured. After the completion of these operations, the required test pressure was created by a manual hydraulic press and the plunger (position 4), and measurements were taken.

To assess the friction from the movable inner cylinder in the bearings and the mechanical seal at different pressures, the viscometer was equipped with a zero-length rotor (position 8). The viscometer was also equipped with a calibration disk (position 7) and a set of weights (position 11). With the help of the calibration disk and weights, experiments were performed in the constant torque mode, $M = const$, and calibration of the torque meter (TM) was accomplished.

The development of a TM was difficult. Meters based on elastic elements were not suitable due to the expected extreme dependencies and large values of the torque itself. As a result, a TM was developed that converts the torque into hydraulic pressure (Figure 3). The TM rigidity was more than $16.5 \cdot 10^3 \text{ Nm/rad}$, which made it possible to record any dependencies of the torque on the shear rate, time, *etc.*

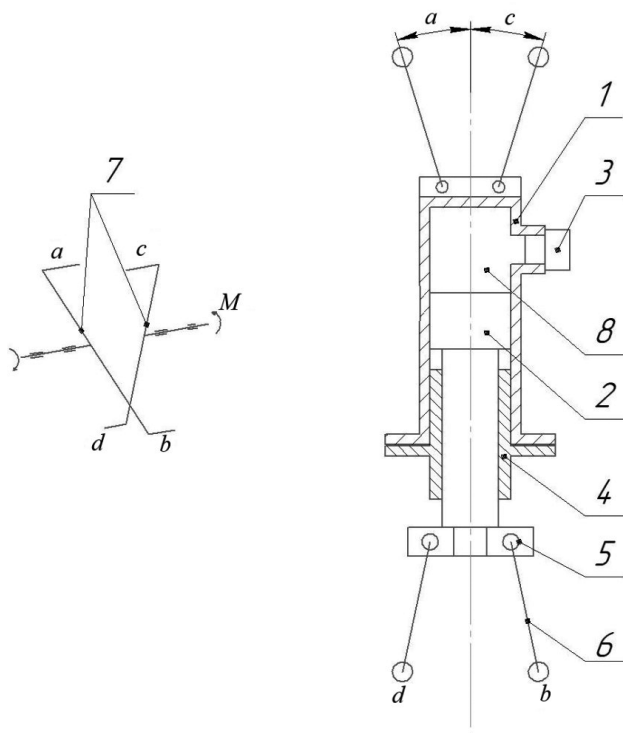


Figure 3. Torque meter (TM): 1 – hydraulic cylinder barrel, 2 – plunger, 3 – pressure sensor, 4 – guide bushing, 5 – traverse with hinges, 6 – rod with hinges, 7 – crosspiece with pins, 8 – oil

Structurally, the TM was a plunger hydraulic cylinder, in which traverses, with two holes in each, were made at the end of the hydraulic cylinder and on the plunger rod (position 5). Two crosses (position 7) with pins (two on the crossbars of the crosspieces) were introduced into the drive kinematic chain. The hydraulic cylinder was placed between the crossbars and the articulated rods (position 6) and connected to the pins of the crosspieces. The connection diagram is shown in Figure 3. During rotation, the circumferential force through the rods (position 6) results in hydraulic pressure in the liquid (oil), which is directly proportional to the value of the torque, and which is recorded by the sensor (position 3).

The TM was preliminarily calibrated with the help of a calibration disk and a set of weights, with the corresponding dependence recorded. In this research, an oscilloscope was used as a secondary device, and this calibration table was saved on the oscillogram for each experiment.

3 Determination of GP Characteristics on a Capillary Viscometer

3.1 Determination of the GP flow stress

The fact that GP is a viscoplastic medium is accepted in the powder industry. Otherwise, it would be impossible to press out any powder elements with the correct geometric shape. However experimental studies for determining the flow stress and its value have not been carried out. It is because of the presence of the shear stress that the established technology for single-base smokeless powder production could not be used. Therefore, the determination of the shear stress is of scientific interest.

When the value of the shear stress (τ_0) of a viscoplastic medium is exceeded, shear flow commences. However registration of the start of the flow presents a difficulty. It is easier to determine the end of the flow [2]. Experiments to determine the presence and value of the shear stress were carried out using two corrugated capillaries with diameter $6.65 \cdot 10^{-3}$ m and lengths $l_{sh} = 20 \cdot 10^{-3}$ m and $l_1 = 60 \cdot 10^{-3}$ m.

A viscometer unit with a capillary equipped with a prepared GP was installed in the “UMM-5” and pressing was performed at the lowest speed. When the GP cord emerged from the support (Figure 2, position 3), the drive of the tensile testing machine was stopped, the outflow pressure was recorded, and its decrease was observed. The physical aspect of the experiment was based on the specific force-measuring system of the “UMM-5” tensile testing machine. Its developed effort was compensated by the deflection of the pendulum (Figure 1, position 6) from the vertical position. When the drive stopped, the pendulum tried to return to its original vertical position, and, with a decreasing force, pressed on the viscometer unit. In theory, the residual pressure should become stabilized upon reaching a pressure equivalent to the value of τ_0 in the capillaries.

Figure 4 shows the dependence “force vs. time” $F = f(\tau)$ for short and long corrugated capillaries. Curve 3 is the curve of the difference between curves 1 and 2. Its appearance more accurately determines the residual outflow pressures, which characterize the shear resistance of the GP structure at $j = 0$, the holding time (T) should be increased maximally. When working with GP, it is necessary to take into account the high volatility of the alcohol-ether solvent, which shrinks the powder cord in the capillary. It can cause a change in the recorded force not related to the strength of the GP structure. Since solvent losses are always observed, it is desirable to reduce the holding time T . Since in experiments to determine the values of τ_0 , the goal is to achieve a constant difference in outflow pressures at $j = 0$ for both capillaries. To ensure these mutually exclusive requirements, a curve of the difference between curves 1

and 2 is constructed.

As the experiments showed, the curve of the difference between curves 1 and 2 is guaranteed to become a straight line, $\Delta F = const$ at a time value $T \geq 12 \cdot 10^2$ s for all of the investigated GPs. Based on the differences in the values of ΔF , taking into account the diameter of the mould, the differences in outflow pressures (ΔP) for both capillaries was calculated. The value of the shear stress was determined by the Equation 1:

$$\tau_0 = \Delta P \cdot d / 4 \cdot \Delta l \quad (1)$$

where τ_0 is the shear stress (Pa), ΔP is the difference in the outflow pressure from two capillaries, of different lengths but with the same diameters, when the outflow process is stopped (Pa), d is the diameter of the capillaries (m) and Δl is the difference in capillary lengths (m).

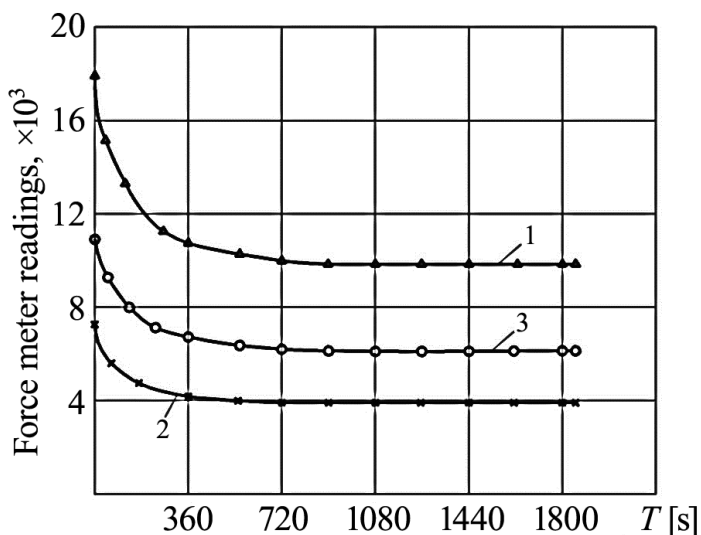


Figure 4. Measurement of the flow force after stopping the viscometer drive: 1 – for a long corrugated capillary, 2 – for a short corrugated capillary, 3 – difference between graphs 1 and 2

For reliability, the experiments were carried out with 8-10 parallel measurements. The spread in the values of τ_0 in parallel experiments was estimated by the coefficient of variation (K_v). GP batches were made with different contents of the alcohol-ether solvent in the GP and with different solvent activities, which corresponded to the real indicators in gunpowder

production. K_v is the coefficient of variation. The results of the experiments are presented in Table 1.

Table 1. Values of shear stress for various batches of GP

GP batch	Nitrogen content [%]	The amount of solvent in relation to the weight of nitrocellulose [%]	Alcohol-ether ratio	$\tau_0, \times 10$ [MPa]	K_v [%]
Guncotton No. 1	13.4	95	1:1.88	1.10	1.77
				0.91	2.77
				1.20	1.53
	13.5	100	1:2.10	0.49	6.84
	13.0	75	1:1.75	2.25	1.28
	13.27	85	1:1.77	2.03	1.12
				1.38	2.51
13.25	82	1:1.85	1.77	1.90	
13.3	89	1:1.82	1.88	6.06	
13.38	94	1:1.81	1.10	7.10	
Guncotton No. 2	12.2	68	1:2.28	1.14	2.30
				0.86	13.60
	12.4	75	1:1.82	1.88	1.98
1.36				4.00	

As can be seen from Table 1, the values of the shear stress for different batches of GP are different. With a decrease in the solvent content, the value of τ_0 increases. The value of the shear stress for guncotton No. 1 GP is higher than for guncotton No. 2 GP. For separate batches of guncotton No. 1 and guncotton No. 2 they are close in value.

In this research, an attempt was made to increase the holding time T up to 20-23 h. In this case, the sliding bearing was additionally sealed with polyethylene film. The values of the shear stress decreased. The values obtained are presented in Table 2.

Table 2. Value of GP shear stress at long holding time

GP batch	Nitrogen content [%]	Solvent content [%]	Holding time T [h]	$\tau_0, \times 10$ [MPa]
Guncotton No. 1	13.45	97.7	20	0.67
	13.2	80.0		0.58
	13.1	78.7		0.32
Guncotton No. 2	12.3	81.9	23	0.62

But as was shown by visual inspection of the GP samples extracted from the capillaries, such sealing does not eliminate solvent leaks. The pulp undergoes shrinkage and therefore the test results are not correct.

3.2 Determination of GP flow curves

The determination of the regularities of the GP flow in the capillaries was carried out according to the previously indicated method, using corrugated capillaries with a diameter of $6.65 \cdot 10^{-3}$ m and length $20 \cdot 10^{-3}$, $60 \cdot 10^{-3}$ and 0.0 m. Experiments were performed with guncotton No. 1 pulp (nitrogen content $\sim 13.1\%$) and guncotton No. 2 pulp (nitrogen content $\sim 12.7\%$). At the same time, when determining the “pressure-flow” dependence for the capillaries, the value of the shear flow was also determined according to the method described above. The rheological properties of the GPs were determined based on the production specifications for several GP batches.

The results of the experiments to determine the pressure-flow rate dependence on the corrugated capillaries for the GPs for batches of guncotton No. 1 and guncotton No. 2 showed that the dependence $P = P(Q)$ for the GPs for both short and long capillaries is not monotonic (Figures 5 and 6).

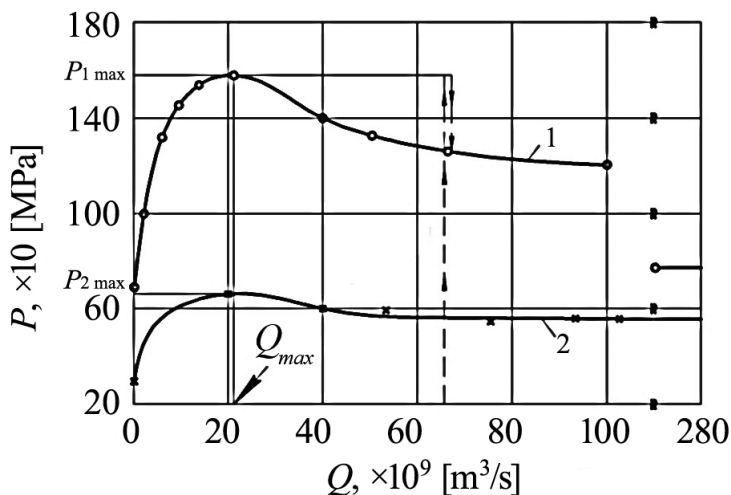


Figure 5. Dependence of “flow-pressure” for a pair of corrugated capillaries for guncotton No. 1 pulp: 1 (○) – long capillary; 2 (×) – short capillary

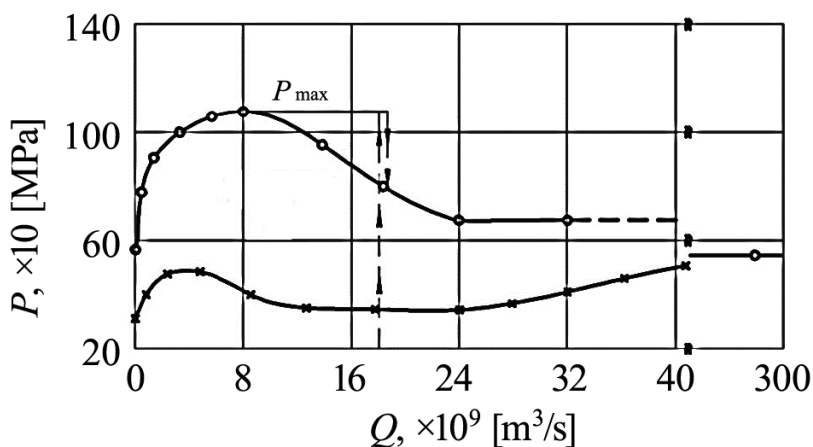


Figure 6. Dependence of “flow-pressure” for a pair of corrugated capillaries for guncotton No. 2 pulp: (○) – long capillary; (×) – short capillary

An increase in the flow rate through the capillary leads to an increase in the outflow pressure, but this increase only occurs up to a certain flow rate (Q_{max}). With a further increase in flow rate through the capillary ($Q > Q_{max}$), the pressure starts to decrease. The nature of the dependence $P = P(Q)$ for values of $Q > Q_{max}$ was the same for all GPs. There was a weak dependence of the outflow pressure on the flow rate through the capillary. Within a certain range of flow rates, the dependence of $P = P(Q)$ became linear, $P \approx const$, after which an unstable flow regime occurred, characterized by fluctuations in the flow pressure.

In the Figures 5 and 6, the area of unstable flow is shown by a dotted line. The area of unstable flow ends with a drop in outflow pressure, the value of which changes weakly with increasing flow rate. The pressure is shown after the graph breaks. When determining the outflow pressure at $Q > Q_{max}$, the pressure first increased to the value of P_{max} , then decreased to the steady state. This is shown by vertical dashed lines with arrows on the graphs (Figures 5 and 6). For guncotton No. 2 pulp, in some batches, after $Q > Q_{max}$ there was a slight increase in the outflow pressure. The sections of the $P = P(Q)$ dependence also changed the appearance of the GP cord outlet from the corrugated capillary. The surface of the cord gradually changed from the herringbone pattern into a smooth one. The moment when the appearance of the cord surface changed corresponded to the unstable flow regime and ended with a pressure drop. By disassembling the corrugated capillaries, it was found that when the surface of the cord passed from the “herringbone” appearance to a smooth surface, for most of the length

of the capillary the GP in the thread is separated from the central core of the cord. The GP spiral and the centre bar exist separately and are not connected back. There is a “breakdown” of the pulp from the corrugations of the capillaries.

Analysis of the literature on the study of rheological properties shows that the dependencies obtained for $P = f(Q)$ fully coincide with similar dependencies for plastic dispersed systems [3, 7]. However, their non-monotonic nature due to structural transformations, as in all other plastic dispersed systems, complicates further processing of the experimental data.

The use of the methods of capillary viscometry (Bagley’s correction, the method of two capillaries), due to the non-monotonic nature of the dependence of $P = P(Q)$, is inappropriate, since the flow curves calculated by these methods do not reflect the physical essence of the processes occurring in the GP during its deformation. However, since the dependence of $P = f(Q)$ for both capillaries are monotonic up to P_{max} , it makes sense to represent the dependence of $P = f(Q)$ in the form of averaged flow curves, $\tau = f(j)$.

Figures 7 and 8 present the results of the averaged flow curves $\tau_R = f(j_{av})$. The j_{av} values should be considered conditional, since the distribution of the shear rate along the radius of a corrugated capillary is generally unknown [3, 7].

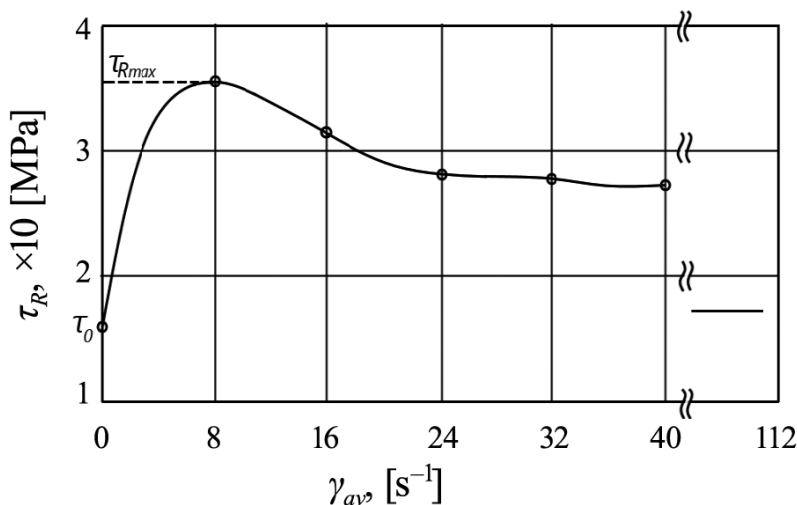


Figure 7. Average flow curve of guncotton No. 1 pulp

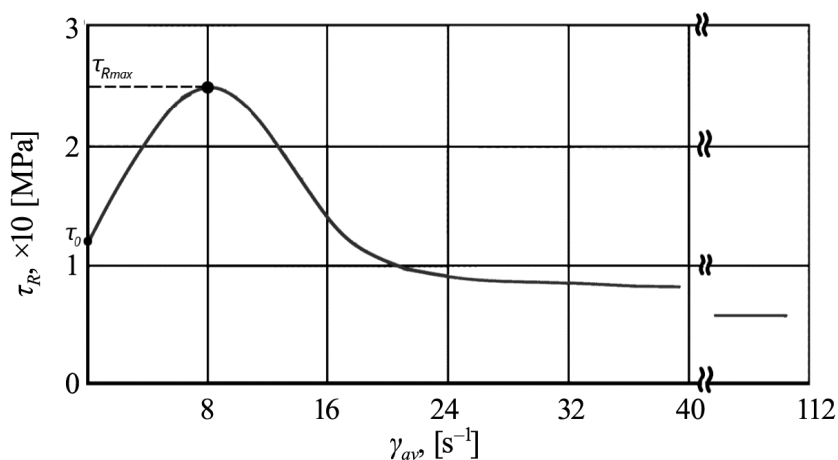


Figure 8. Average flow curve of guncotton No. 2 pulp

Analysis of these graphs of the averaged flow curves of the GPs shows that these curves have a maximum in stress (points τ_{Rmax}), after which a weak dependence of stress on the strain rate gradient (conditional) is observed. In a similar manner to the dependence of $P = P(Q)$, the curves for $\tau = f(j_{av})$ have an unstable flow area, after which the flow regime changes.

The representation of the section of the curve from τ_0 to τ_{max} in logarithmic coordinates shows that this section can be described by the Herschel-Bulkley equation. In this case, these equations are:

$$\text{– for guncotton No. 1: } \tau_R = 1.76 \cdot 10^5 + 1.32 \cdot 10^5 j_{av}^{0.133} \quad [\text{Pa}] \quad (2)$$

$$\text{– for guncotton No. 2: } \tau_R = 1.23 \cdot 10^5 + 0.389 \cdot 10^5 j_{av}^{0.55} \quad [\text{Pa}] \quad (3)$$

When conducting these rheological experiments, a large number of batches of GP were investigated. For all of the investigated batches, the shape of the flow curves was the same, the differences were quantitative. The values of the coefficients K and n , determined on a capillary viscometer $P = P(Q)$ for different batches, were different. Table 3 lists the coefficients K and n for some of the investigated batches.

Table 3. Constants of the rheological equation for different batches of GP

GP batch	Nitrogen content [%]	$K, \times 10^5$ [Pa·s]	n
Guncotton No. 1	13.5	0.59	0.115
	13.4	0.32	0.142
		0.43	0.130
		0.46	0.111
		0.33	0.500
	13.38	0.48	0.132
	13.3	0.35	0.300
	13.0	0.52	0.080
	13.27	0.48	0.370
		0.39	0.070
13.25	0.38	0.050	
Guncotton No. 2	12.4	0.48	0.051
		0.28	0.110
	12.2	0.44	0.077
		0.43	0.067
		0.42	0.083

When determining the flow curve of a GP, in addition to the specified features two more distinctive features were established. The first was that the flow curves $\tau_R = \tau(j_{av})$ obtained on different capillaries are not invariant. Figure 9 shows the GP flow curves obtained on capillaries of various sizes. All of the curves were determined on the same batch of GP. Curves 1 and 2 are the results of parallel experiments. These data show that the discrepancy between curves 1 and 3, and between curves 1 and 4, is more significant than between curves 1 and 2.

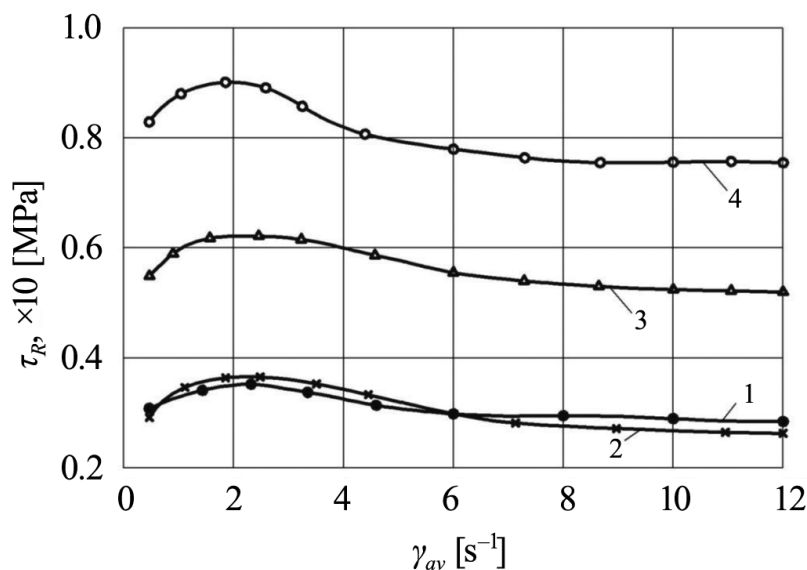


Figure 9. Non-invariance of GP flow curves for diameter $d = 6.65 \cdot 10^{-3}$ m:
 1, 2 – parallel experiments, capillary sizes $l_1 = l_{sh} = 60 \cdot 10^{-3}$ m,
 3 – capillary sizes $l_1 = 60 \cdot 10^{-3}$ m, $l_{sh} = 0$ m,
 4 – capillary sizes $l_1 = 20 \cdot 10^{-3}$ m, $l_{sh} = 0$ m

An explanation of the behaviour of plastic dispersed systems during their shear flow is given in [7, 8]. Applying these regularities to GP flow, the following features of the GP flow curves were obtained, namely, the presence of the shear stress, maximum stress, weak dependence of τ_R on j_{av} .

According to the values of τ_{Rmax} , a change in the outflow mode at a certain j_{av} value due to the processes of structural transformations occurring in GP during its deformation. However, as the value of the shear stress approaches the value of maximum stress, the structural transformations in the GP intensify, and at the moment of reaching the maximum stress, the GP structure loses its strength. In the range of values $\tau_0 - \tau_{Rmax}$, orientation of the guncotton fibers occurs, and by the time τ_{Rmax} is reached, most of the fibers are oriented in the direction of shear (the structure of the powder as such is formed), and since the dispersed phase gluing the fibers of guncotton No. 1 together cannot show significant shear resistance, then, beyond the value of τ_{Rmax} , the phase boundary between the GP in the corrugations and the main bar begins to form. The stress values decrease, and, in fact, the process of sliding the GP along with the GP, along with the lubricant from a solution of nitrocellulose in an alcohol-ether solvent, is observed.

When studying the flow of plastic dispersed systems, the question of the depth of structural transformations always remains open. For GPs, some conclusions can be drawn from an analysis of the appearance of the cords obtained at different flow rates through the capillary. With an increase in the flow rate, the depth of the ruptures of the surface of the GP cord decreases, and its appearance changes. So, the process of destruction of the GP structure is shifted to the walls of the corrugated channels, to the zone of maximum stress.

Moving on to quantitative estimates of the results of studying the shear flow of GPs, it should be noted that all of the measurement results for the rheological properties of a GP should be considered qualitative. The values of the rheological parameters of a GP depend on the prehistory of the deformation of the GP before it contacts the measuring surfaces. These are the deformation of the GP in the inlet zones of the capillaries, deformation in the capillaries, deformation of the GP when loading into the viscometer, *etc.* That is, almost always there is a medium with intermediate values in the range of τ_0 - τ_{Rmax} . Hence, the non-invariance of the GP flow curves obtained on different capillaries. Even with this correction taken into account, the shear flow of a GP is specific.

The shear flow of a GP occurs in a very narrow range of stresses. For example, in the studied batches, the range of stress values from τ_0 - τ_{Rmax} did not exceed 0.35 MPa. The form of the dependence of $P = P(Q)$ for a GP depends on the level of the operating pressures. For long capillaries, the $P = P(Q)$ dependency has a pressure maximum more pronounced than for short ones. A GP also loses strength at low values of conditional deformation rates (in the investigated batches j extra. ≈ 8 - 10 s⁻¹), and the outflow mode is changed at $j_{av} \approx 100$ - 120 s⁻¹. Shear flow of a GP is more similar to the flow of solids than of liquids. The results obtained from the point of view of the methodology for conducting rheological studies on GP allow the conclusion that constant pressure capillary viscometers are of little use for studying the shear flow of GPs. With their use, it is possible to obtain flow curves only in the range from τ_0 to τ_{Rmax} .

The results of this investigation of the regularities of the shear flow of GPs using capillary viscometry can be presented in the form of a generalized flow curve, in which the quantitative indicators depend on the type of capillaries used and the shear rate gradient indicator is arbitrary, since in the general case the shear rate distribution over the capillary cross-section is unclear. This generalized flow curve has four sections (Figure 10). The first section is from τ_0 to τ_{Rmax} , the second section is a drop in the stresses, the third is an area of unstable flow of the GP, and the fourth is an area of sliding of the GP.

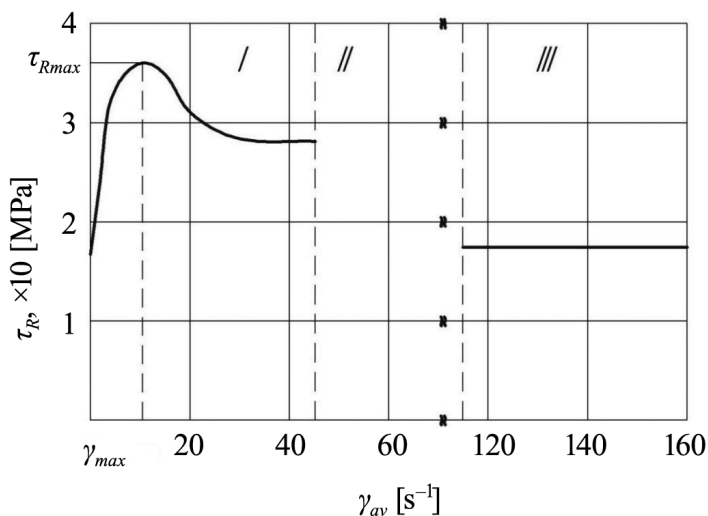


Figure 10. Generalized flow curve of a GP, obtained by capillary viscometry

4 Conclusions

- ◆ As a result of the experiments carried out, the presence of shear stress in guncotton pulp (GP) can be considered a fact. GP should be classified as a viscoplastic medium.
- ◆ The dependence “flow *vs.* pressure” for GP is non-monotonic and has a maximum pressure.
- ◆ The pressure of the GP outflow from corrugated capillaries when passing through the maximum decreases to a steady state. With a further increase in the flow rate through the capillary, there is a transition from shear flow to sliding. In this case, the outflow pressure first fluctuates, then decreases to a steady-state, which then weakly depends on the change in flow rate.
- ◆ Due to the non-monotonic nature of the $P = P(Q)$ dependence for GP, the construction of flow curves $\tau = \tau(j)$ from them is not correct, since these flow curves do not reflect the physical processes occurring in the GP during shear flow.
- ◆ When constructing the flow curve in the section from τ_0 to τ_{Rmax} , the flow curves of the GP are described by the Herschel-Bulkley equation:

$$\tau = \tau_0 + K \cdot j^n$$

- ◆ The flow curves of the GP obtained on corrugated capillaries of different sizes are non-invariant and depend on the magnitude of the deformation of the GP in the capillaries.
- ◆ GP flows in a narrow range of pressures and deformations. The developed shear flow is uncharacteristic for the GP, and the shear deformation of the GP ends with the loss of continuity and the transition from flow to sliding along the phase boundary.
- ◆ All quantitative measurements of the rheological properties of GP by capillary viscometry should be considered a special case and depend on the characteristics of the viscometers.

References

- [1] Marchenko, G.M.; Zabelin, L.V. *Production of Cellulose Nitrate. Physicochemical Fundamentals of Cellulose Nitrate Processing*. TsNIINTI I TEI, Moscow, **1988**, pp. 154-155.
- [2] Veschev, A.A. About Wall Sliding of Asbestos during Extrusion. *Proc. Yaroslavl Polytechnic Institute*, Yaroslavl, **1972**, 34: 124-130.
- [3] Pavlov, V.P.; Vinogradov, G.V. Generalized Rheological Characteristics of Plastic Dispersed Systems. *Colloid J.* **1966**, 28(3): 424-430.
- [4] de la Ossa, F.; Angeles, M.; Torre, M.; Carmen, G.-R. Nitrocellulose in Propellants: Characteristics and Thermal Properties. *Adv. Mater. Sci. Res.* **2012**, 7: 201-220.
- [5] Terner, R.V. *The Main Processes of Polymer Processing. Theory and Methods of Calculation*. Chemistry, Moscow, **1972**, 453.
- [6] Wei, R.; He, Y.; Liu, J.; He, Y.; Mi, W.; Yuen, R.; Wang, J. Experimental Study on The Fire Properties of Nitrocellulose with Different Structures. *Materials* **2017**, 10(3), paper 316: 1-16.
- [7] Vinogradov, G.V.; Klimov, K.I. *Creep and Shear Strength of Lubricants*. (in Russian, ed. trans.) Reports of the USSR Academy of Sciences. **1950**, 71(4): 697-701.
- [8] *Gunpowder, Explosives and the State: A Technological History*. (Buchanan, B.J., Ed.) Aldershot, Ashgate, **2006**, 449; ISBN 0-7546-5259-9.

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