was found using bias-belted tires.

These experimental studies demonstrate that the rubber vulcanisate properties reach an optimum at an *RF* that is attributed to the combined carbon black properties of structure and AMD or N_2SA. Furthermore, the relationship between the *RF* and rubber vulcanisate properties remains the same irrespective of oil loadings (5 phr oil/50 black-SBR 1500, 0 phr oil/50 black-ASTM NR, and 70 black/48 phr oil-SBR 1712). The *RF* at 50 phr loadings obtained in an EPDM matrix is, therefore, a useful parameter to characterise the combined properties of carbon blacks. It also appears that the transition point at which the reinforcement factor rises rapidly in relation to loadings is the optimum loading for that particular black.

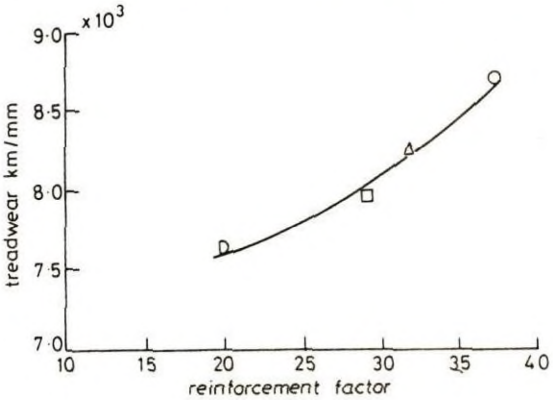

Fig. 20 Treadwear against r.f. Applied pressure 16·18 MPa, L/D 15, temperature 190°C

o N234
Δ N220
□ N339
D N347

5 Conclusion

An experimental technique has been presented to characterise carbon blacks using a constant-force capillary rheometer. Best results were obtained when the extruding pressure was below the critical fracture stress of the virgin polymer. Results presented demonstrate that the *RF* characterises, as a single entity, the combined properties of structure and particle related parameters-N_2SA and AMD. A functional relationship is also shown between *RF* and the rubber vulcanisate properties obtained in different polymer systems (SBR 1500, SBR 1712 and NR).

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The contribution of wall slip in the flow of rubber

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Abstract: Experiments in a rheometer using smooth and grooved rotors have shown that substantial wall slip can occur between rubber and smooth metal surfaces which is probably caused by a lubricating layer. The behaviour of this lubricating layer with reference to shear stress, hydrostatic pressure and temperature has been examined. This work also shows that the mechanism of shear flow changes at high shear stresses which will give rise to what is apparently another type of wall slip when the stress is at its highest at the metal surface.

1 Introduction

The rheological behaviour of rubber formulations has been assessed in the rubber industry almost entirely by the Mooney viscometer. This instrument operates normally at a low shear rate of 1 reciprocal second, which is well away from the shear rates encountered in factory processing. It is increasingly apparent that many occurrences in factories are not explained by such single-point data. Occasionally capillary extrusion rheometers, which give more extensive data, are used, but there are problems in obtaining consistent behaviour. The shear-stress/shear-rate results plotted logarithmically frequently give changes in slope. Dies of the same length-to-diameter ratios should, according to classic theory, give the same shear-stress/shear-rate characteristics, but often large deviations are found. Wall slip has been recognised as one cause. Worthy and Helmy using capillaries with three different diameters have deduced wall slip velocities for plastic materials.[1]

There is clearly a need in the rubber industry for a rheometer that gives more comprehensive data and is more convenient to use.

2 T.M.S. rheometer

The basic configuration of the Mooney viscometer has advantages in rheological testing. The sample has a geometry set by the cavity and rotor and the sample can be conditioned by shear, prior to measurements to eliminate thixotropic effects. It has a heavily serrated rotor to eliminate wall slip, but in most processing situations the interaction between rubber and smooth surfaces is more relevant. To have reproducible results in such situations it is necessary to have a fresh rubber surface coming into contact with the rotor and to be able to control pressure. The procedure adopted was therefore one used for making precision rubber mouldings in the factory. A transfer system was built on top of the Mooney cavity, according to the layout in Fig. 1.

This has the following advantages:

(i) The pressure in the cavity is controlled by the force applied to the injection ram

(ii) Fresh rubber surfaces make contact with the rotor and cavity

(iii) The cavity is always closed during filling and maintains precise dimensions

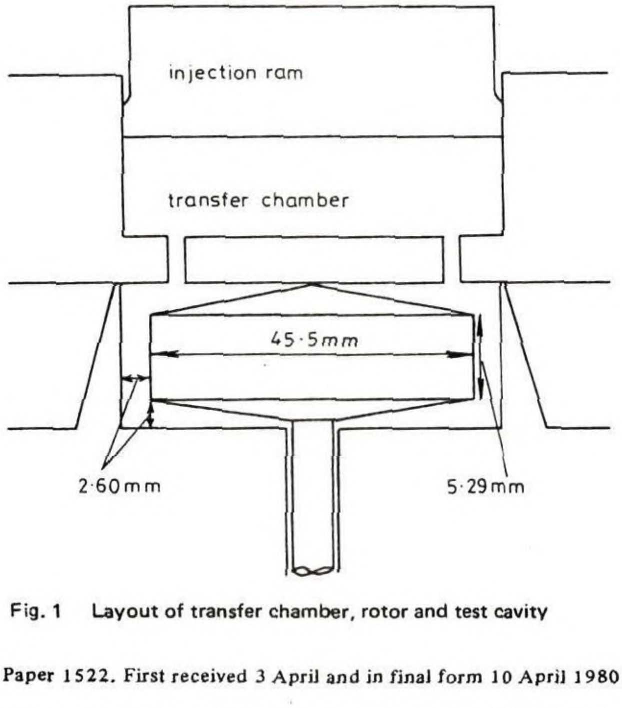

Fig. 1 Layout of transfer chamber, rotor and test cavity

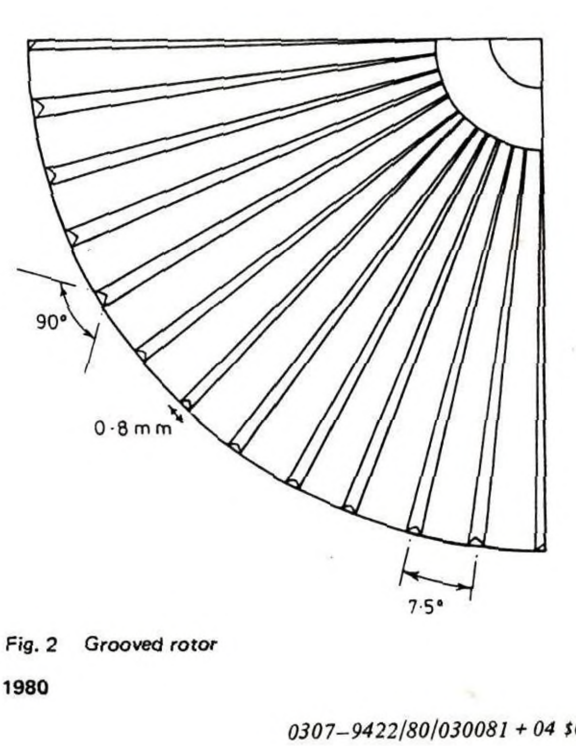

Fig. 2 Grooved rotor

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(iv) A single cylindrical blank is required so results are hardly influenced by operator skill

(v) Prewarming in the transfer chamber followed by injection enables a uniform temperature to be established more rapidly.

Three rotors were obtained for the machine:

(*a*) With 48 radial grooves on each face according to Fig. 2

(*b*) Ungrooved ground surface (Rockwell C Min 60)

(*c*) Polished surface

The faces of the rotor are biconical with an angle of 6° 40′ giving a shear rate of 0·895 reciprocal seconds at 1 rev/min. The clearance between the outer circumference of the rotor and the walls of the cavity provides the same shear rate. The cavity is the standard Mooney cavity with heavy grooving. This particular machine is fitted with a variable-speed motor and a gearbox giving a rotor speed range of 1 to 40 rev/min. It also has the capability of measuring recovery, stress relaxation and stress development during start up.

3 Results

With the use of this equipment to obtain shear-stress/shear-rate responses, it was found that choice of rotor had dramatic effects. Fig. 3 illustrates examples of extreme cases. Material A which was a raw Butyl rubber gave the same response regardless of rotor, and it was not possible to draw separate lines. Material B which was a nitrile rubber formulated with a high loading of plasticisers and filters produced enormous differences between the grooved and the other two rotors, a factor of 8–12 in stress or 180–200 in strain rate. These differences are ascribed to wall slip.

Wall slip velocities and shear rates are calculated from the results on the grooved and polished rotors at a given shear-stress level according to the formulas:

$$\text{wall slip } V = 2\pi r\,(S_p - S_g) \qquad (1)$$

$$\text{shear rate } \dot{\gamma} = 2\pi r\, S_g/d \qquad (2)$$

where

S_p and S_g are the rotor speeds for the polished and grooved rotors

r is the radius to the rotor edge and

d is the clearance between the rotor edge and cavity wall.

An extensive study was carried out on a fully formulated EPDM mix containing high levels of carbon black and oil. The results for a range of temperatures are shown in Fig. 4 plotted linearly as wall-slip velocity against shear stress. The effect of pressure on shear and wall-slip response on a similar rubber is shown in Fig. 5. Applying 10 MN/m^2 hydrostatic pressure reduces wall-slip velocities by around 20%. Up to 3MN/m^2 pressure reduces shear rate by around 15% at the lower shear stresses but there was a dramatic 2·5 to 1 reduction in shear rate at the highest shear stress. Further increases in pressure had little effect.

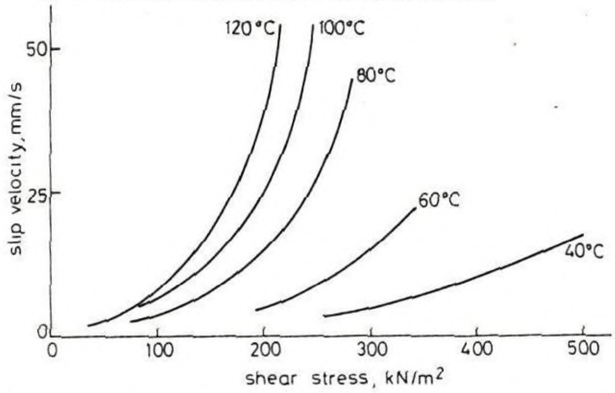

Fig. 4 Effect of shear stress and temperature on wall slip with a formulated EPDM

4 Mechanisms of wall slip

It is suggested that the wall slip manifested by the differences in rotational rate between the grooved and ungrooved rotors is due to the presence of a thin lubricating layer. Such a layer is likely to be formed by one or more of the added ingredients.

It is assumed in eqn. 1 that there is no wall slip with the grooved rotor. The shape of the log shear-rate responses with the grooved rotor on a rubber showing wall slip is very similar to that where there is no wall slip, i.e. there is no increase in gradient in the 1 to 10 rev/min range. It is believed that the grooves are sufficient to break the continuity of the lubricating layer. Possibly a small amount of slip does occur, but the rotor speed at a given stress when wall slip occurs is so much greater with the ungrooved rotors that the errors are small.

A master curve can be produced from the data in Fig. 4 by applying shift factors to the slip velocities according to the temperatures. A similar master curve can be produced for shear rate and the two are shown as log/log plots in Fig. 6. As can be seen the gradient for shear rate is much higher than that for wall slip velocity. Thus at high stresses the relative influence of wall-slip on rotor rotational speed declines and so the responses shown in Fig. 3 for the grooved and ungrooved rotors converge.

The (log-stress) (log-rev/min) response for gum Butyl levelled out almost completely at high rates. Such behaviour

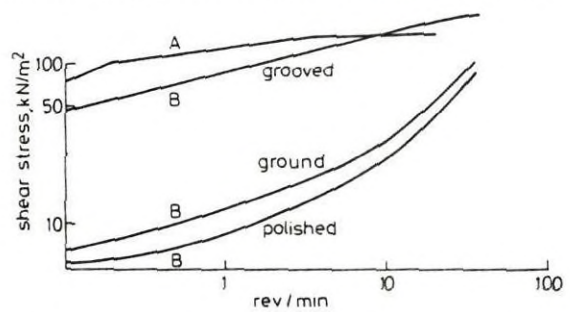

Fig. 3 Effect of rotor type and rev/min on shear stress at 100°C
A = Gum Butyl (all 3 rotors)
B = fully formulated nitrile

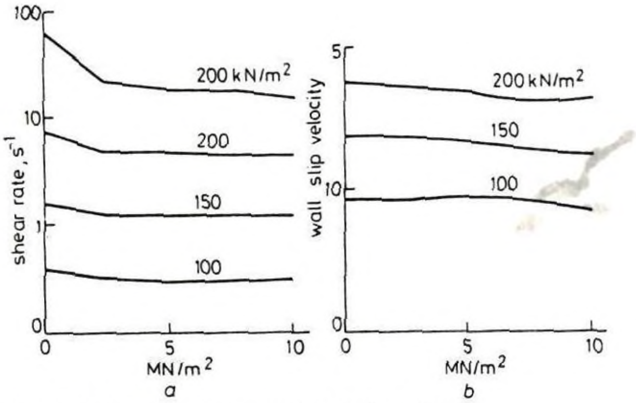

Fig. 5 Effect of cavity pressure at various stresses
(*a*) on shear rate
(*b*) on wall-slip velocity

has been identified with fracture by Turner, Moore and Smith.[2]

The independence of rate suggests that the energy is used to provide cyclical elastic deformation followed by fracture and little energy is lost by viscous flow. Such a flow characteristic can give a different type of wall slip when the stress in the rubber is at its highest at a surface. If the cavity of the t.m.s. machine is filled with one semicircle of white rubber and one of black rubber, at low rates laminar shear flow occurs and a series of black and white spirals or layers are built up. At higher rates irregular zones of black and white develop between the conical surfaces and the top and bottom of the cavity, but in the Couette region on the perimeter there is little movement of the bulk of this rubber and a thin grey layer develops adjacent to the rotor. The rotor is 10% smaller in diameter than the cavity and so the stress at the rotor edge is 20% higher than at the cavity wall. In Fig. 3 for Butyl rubber the index defining the gradient in the region of 10 rev/min is 0·05 at most, which would cause the shear rate in the boundary layer to be 40 times that of the rest of the material. Hence the appearance of wall slip.

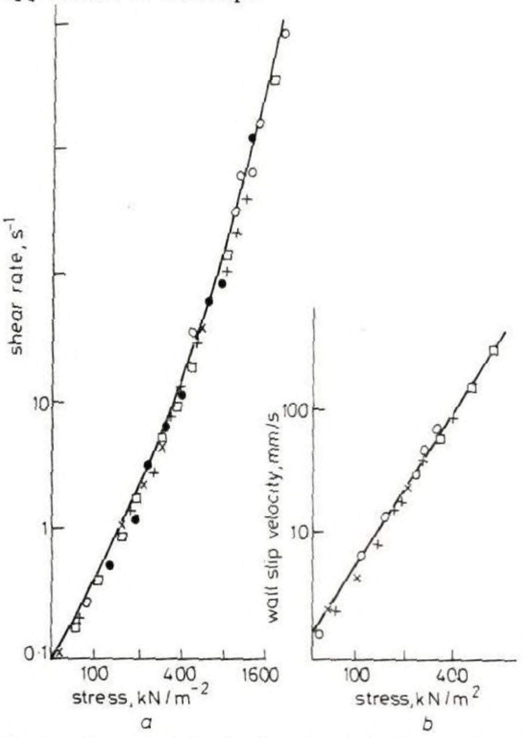

Fig. 6 Characteristics for fomulated EPDM transformed at 100°C
(a) shear rate against stress
(b) wall-slip velocity against stress

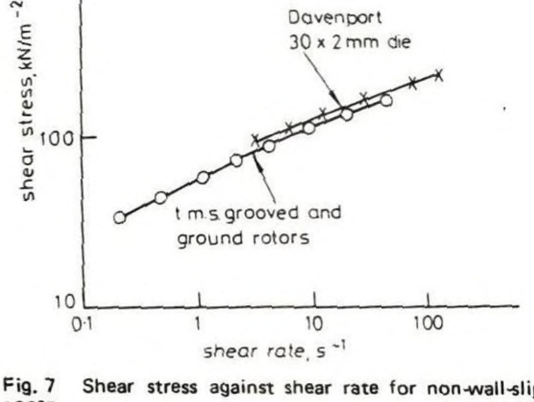

Fig. 7 Shear stress against shear rate for non-wall-slip rubber at 100°C

5 Application of wall-slip data

Tests are often called for at high shear rates to correlate with factory processes such as the flow in runners during injection moulding. Rubbers suitable for this process are usually formulated so that they exhibit wall slip. The effect of wall slip on volumetric flow of a non-Newtonian fluid in a capillary is shown by eqn. 3:

$$Q = \pi r^3 \dot{\gamma}\, n/(3n+1) + \pi r^2 V \qquad (3)$$

where

$\dot{\gamma}$ = shear rate of the rubber in contact with the lubricating layer at the wall

r = radius of capillary

n = power law index

V = wall slip velocity.

$\dot{\gamma}_A$ is the present shear rate which is the parameter normally used in the presentation of capillary results and is the shear rate defined by eqn. 4:

$$\dot{\gamma}_A = 4Q/\pi r^3 \qquad (4)$$

$$\dot{\gamma}_A = 4n\dot{\gamma}/(3n+1) + 4V/r \qquad (5)$$

Eqn. 5 shows how the apparent shear rate depends on the Rabinowich correction for power law flow and on wall slip.

Fig. 7 shows shear-stress/apparent-shear response for a non-wall-slip material obtained in the t.m.s. rheometer and a Davenport capillary rheometer with a 30mm x 2mm die. The slopes and absolute values coincide well. A similar plot in Fig. 8 for a high-wall-slip material shows the capillary result to be similar in slope to the ground rotor but displaced. Using the t.m.s. results and eqn. 5 the capillary result can be predicted and is shown by the dotted line in Fig. 8. It is still not in the correct position. One cause of the discrepancy could be that the die had a rougher finish than the ground rotor but this is unlikely. Possibly the low bulk to surface area of the rubber in the capillary led to a thinner lubricating layer and consequently less slip owing to shear in the layer.

Wall slip has its greatest importance in flow in small channels such as runners in injection-moulding machines, and it is important not to overestimate its effect where large dimensions and velocities are concerned. For example, a calculation shows that 10% of potential shear is lost by wall slip when the EPDM rubber is mixed in a large internal mixer.

Although 10% may seem a small factor, it is sufficient to explain why this performance of an internal mixer declines in the first few weeks of its life as the rotors take on a polish. A more striking example was found when a screw

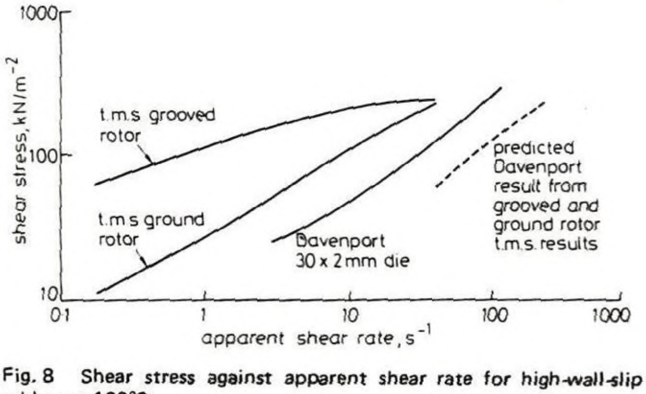

Fig. 8 Shear stress against apparent shear rate for high-wall-slip rubber at 100°C

that had not been adequately polished was fitted to an extruder. While the output was perfectly satisfactory with one material, it was hopeless with another (B in Fig. 3). The good material behaved similarly to A in Fig. 3. With these results it became clear that the output was satisfactory with the first material as it was insensitive to the finish of the screw or barrel whereas material B would have high wall slip against the barrel and hence would progress only slowly along the channels in the screw. This indicated that the correct action to be taken was to improve the polish of the screw, which did eliminate the problem.

6 Discussion

While wall slip had been suspected of affecting the flow behaviour of rubbers, this is one of the first attempts to study it under controlled conditions. It emerges that it is due to certain ingredients in the formulation forming a lubricating boundary layer. More systematic work is needed to identify the specific action of these ingredients. It is also necessary to identify how the thickness of the layer is affected by the bulk of the material providing it. Only three metal surfaces have been studied and more comprehensive work is needed to elucidate surface finish-lubricating layer thickness relationships. When analysing production processes it is at least as important to determine relative velocities between the rubber and metal surfaces as it is to calculate shear rates (real or apparent).

It is difficult to isolate slip from shear in results from capillary rheometers and hence they should not be applied to larger-scale processes in the factory.

7 Conclusion

Wall slip due to a thin lubricating layer between the rubber and metal surface is an important feature of the behaviour of rubber in processing. Its study has been neglected due to lack of suitable equipment. The t.m.s. rheometer has been shown to yield useful information and soon will be commercially available.

Its ability to control pressure is essential as the results show that significant changes in stress do occur when pressure changes.

Resolving flow behaviour into wall slip and shear enables proper comparisons to be made of flow in test equipment and factory machinery.

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Prediction of fibre orientation in moulded components

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Abstract: Flow mechanisms acting during the processing of short-fibre reinforced thermoplastics and of dough moulding compounds introduce inhomogeneous distributions of fibre orientation into the moulded components. It is important for design and quality assurance purposes that the main features of these patterns of fibre orientation, and the consequent effects on material properties and on product performance, should be predicted at an early stage. The principal mechanisms for flow-induced orientation have been examined, and it has been shown that fibre alignment is possible under certain flow conditions. In some cases, alignment may depend specifically on the non-Newtonian character of the composite fluid. The effects of converging, diverging and pipe flows have been considered in detail, as have the results of flow around corners and past obstacles. Application of these results to an injection-moulding configuration of sprue, runners and strip moulds, for which experimental observations of fibre orientation are available, has shown good agreement between prediction and practice. The work provides a basis for developing a method for predicting fibre orientation in complex mouldings.

1 Introduction

Short-fibre-reinforced thermoplastics (SFRTP) and dough moulding compounds (DMC) have considerable potential due to the fact that they can be processed by conventional techniques used for unreinforced thermoplastics, notably by injection moulding. Incorporation of fibres can result in higher stiffness, lower creep and improved dimensional stability. However, it does not follow that all properties are enhanced, and strength, impact toughness, internal stresses and fatigue properties are all intimately dependent on the detailed and local material structure. This structure depends on the flow processes within the melt during processing and, in particular, on the orientation of fibres during mould filling. Mouldings may contain regions of highly aligned fibres and regions with random fibre orientation, and it should be expected that this inhomogeneous structure will influence strength, impact and toughness properties.

Inhomogeneity resulting from processing also complicates characterisation of the mechanical properties of a material and use of laboratory data in component design. This arises because two injection-moulded laboratory test specimens, processed from the same basic materials but having different dimensions, may have significantly different forms of inhomogeneity and different apparent mechanical properties. The two sets of mechanical data may not be easily related to one another, and neither one may be directly related to the properties of material in a component moulded in another geometry.

For the reasons given above, it is desirable that some degree of understanding should be achieved of the flow processes occurring during mould filling. It may then be possible to estimate the general features of the structure of a proposed moulding and its likely performance in service. However, it should be recognised that it is probably impossible, and almost certainly not economically viable, to establish a procedure for making detailed predictions for moulds of complex geometry under a wide range of possible processing conditions. All that should be expected are some general guidelines that can be used to reinforce intuition and experience.

Experimental observations of distributions of fibre orientation have been made by a number of workers for both DMC[1,2] and SFRTP[3–9] and, in some cases, partial explanations have been given for the observed distributions. The present paper extends some previous ideas,[10] and attempts to move towards a predictive capability. The approach is that of fluid mechanics, and reference is made, for example, to streamline patterns and to local streamline directions. This implies that there is steady flow, and this will not be the case, for example, in the final stages of mould filling. However, it is likely that there is a significant period of time in which the flow is approximately steady and during which fibre orientations are induced. The final deceleration phase, as the flow is brought to rest, may be of insufficient duration to disturb these orientations significantly.

It has been claimed[1] that the flow of DMC is 'completely at variance with the behaviour of an ideal fluid', so that conventional fluid mechanics ideas cannot be applied to it. However, the interpretation of data upon which this conclusion is based is, in the view of the author, extremely misleading. The relevant experiments consisted of flow in a pipe of circular cross-section, in which variations in diameter produced regions of contracting and expanding flow. The charge of material was in the form of a thin sheet formed into a cylindrical roll, with pigment between the layers, and the charge was driven by a piston. It was assumed that the layers of pigment, which are initially parallel to the pipe axis, would indicate the streamlines of the subsequent flow. However, in the entry region there is a change of velocity profile from constant velocity across the piston to a significant profile further down the pipe owing to fluid viscosity. This axial change of velocity profile

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