

Calendering of Plastics

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Preface

Calendering is probably the most spectacular operation that the plastics industry has to show, it is also the most expensive in terms of capital investment in machinery and buildings. The net effect is that this process is conducted at a very limited number of centres and it is not readily accessible to students of polymer technology. The short accounts of the process familiar in general textbooks on plastics technology fail to convey a proper sense of the scale of this major industrial activity and, equally important, its unusual degree of dependance on the skill and experience of its technical management and plant operatives. At the request of The Plastics Institute the principal Authors of this Monograph have recorded their own extensive experience of the day-to-day running of a large vinyl calendering plant. By the addition of descriptions of important engineering details and ancillaries and a review of the scanty literature of the subject a reasonably complete account of the production of plastic sheet by calendering has been assembled. The absence of a single text on PVC compounding at the time that this work was undertaken made necessary the inclusion of a brief treatment of this subject, readers may now refer to the companion volume, Vinyl and Allied Polymers, Vol. 2, by G. A. R. Matthews for more details.

Many technological operations have reached a remarkable degree of perfection by evolutionary development. Calendering is a prime example of such a process, its experts are able to make rapid processing decisions of an intuitive nature without recourse to laborious rheological calculations. What theoretical work has been done on the behaviour of polymer melts in calenders has been well recorded elsewhere and was not considered appropriate for detailed re-statement in this essentially practical record. The evolutionary process, however, has occupied more than a century and justified a fairly detailed treatment of the history of the calender.

In order to assist the reader, in the light of the U.K.'s forthcoming changeover to the metric system, approximate conversions of all units to the S.I. system appear in parentheses. It is emphasised here that these are not exact conversions nor are they the proposed equivalent values; they are merely approximate values which should

indicate to the reader the order of magnitude of the relevant S.I. units.

Thanks are due to Messrs. Bakelite Xylonite Ltd for their permission to publish numerous diagrams and photographs of plant at their Manningtree works. I would also like to express gratitude to Dr. M. Kaufman for making available material from his *History of PVC*.

Brunel University, 1970

G.J.L.G

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The History of Calendering

1.1 GENERAL

Very few modern technological processes have sprung complete from their designers' drawing boards owing nothing to earlier developments. Calendering is no exception to this generalisation and the subject has an extended history which can be traced through a number of trades. The art has progressed as rapidly as its economic environment has been able to encourage it, subject to the availability of appropriate engineering techniques and working materials.

The term 'calender' is derived from the same Greek root, κυλινδροσ, as the word 'cylinder', and calendering has long been associated with the use of cylindrical rollers for smoothing and glazing operations in the processing of textiles. This is the meaning given to the word in Johnson's dictionary (1775), and the first reference to calendering¹ in the technical literature available to the Author is a description of a horse driven fabric rolling machine (see Fig. 1.1) which is an obvious development on the ancient box mangle. It is of technical interest in that the rolls in this type of machine are not mounted in bearings. Machines for rolling paper, metals and textiles developed separately in the nineteenth century and it is of interest to note the emergence of a special branch of the foundryman's art concerned with providing the large cast iron rolls for these trades, as typified by Alger's patent of 1811².

1.2 EARLY RUBBER CALENDERS

If the line of development leading to Hancock's 'pickle'³ and the two-roll mixing mill is disregarded, on the grounds that these are examples of mixing machines despite their rollers, then the fabric-coating rubber calender emerges in a form instantly recognisable to a present-day technologist from the work of Edmund Chaffee⁴ in the U.S.A. in 1836; and the diagrams from his patent are shown in Fig. 1.2. Chaffee's 'monster' weighed about 30 tons (~30.5)

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tonnes) and was reported to have a roll face-width of 60 in (~ 1.52 m). This remarkable machine was too far in advance of contemporary rubber technology to be an immediate commercial success, but it set the pattern for the design of these machines for the remainder of the century.

Better and more readily accessible versions of Chaffee's drawings are to be found attached to Pickersgill's patent⁵ of 1836 in the U.K. in which he states they were 'communicated to me by a certain

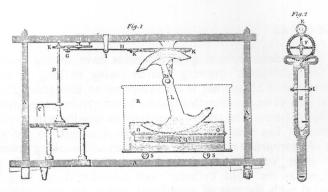


Figure 1.1. Edmund Bunting's prize winning calender mill of 1798. R is the weighted press box and S and S are the rolls. The horse is attached at C

Foreigner residing abroad'. A good account of these ancient cast iron giants is given in Willshaw's Calenders for Rubber Processing⁶, and in Pearson's Rubber Machinery⁷. Thanks to the cooperation of the Director of the Bristol City Museum, enthusiasts may soon be able to see an early British specimen, the 'Iron Duke', which was probably commissioned in 1849 and retired recently from the service of the Avon Rubber Company. A general impression of the arrangement of a rubber calendering plant which was operating in 1882 is shown in Fig. 1.3 and, according to the anonymous author⁸, the machine depicted weighed about 50 tons (~51 tonnes) with each roll weighing between 3 and 4 tons (~3–4 tonnes).

The most remarkable aspect of these early machines was the fact that they remained economically viable for a century, indeed in some cases the original machines remained in production for about this period of time. The great size and capital cost of the machines militated against change; especially remembering that occasional modifications and renovations such as replacing steam engines by electric motors, adding guards to the requirements of the Factory Act (1937), regrinding or cambering roll surfaces, and replacing

E. M. CHAFFEE. Making Rubber Fabrics.

Patented Aug. 31, 1836.

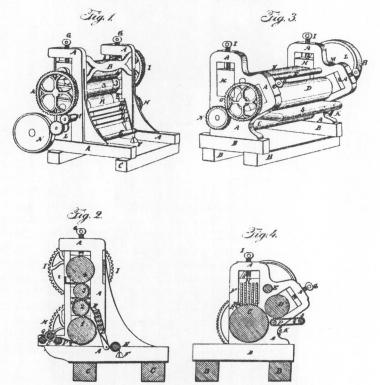


Figure 1.2. Drawings from E. M. Chaffee's patent of 1836

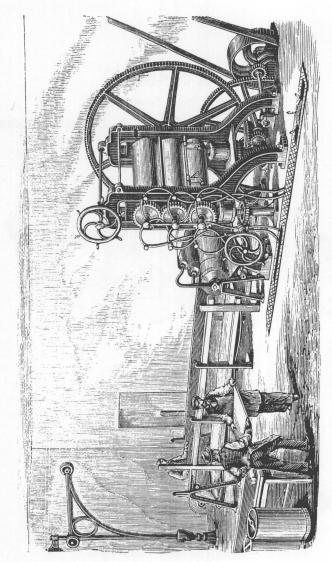


Figure 1.3. Rubber calendering plant of 1882

worn bearings would have sufficed to keep the machine operating adequately.

1.3 CALENDERS AFTER 1930

The incentive to change the early designs came eventually in the 1930s partly because of increases in the standards of tyre building, but more specifically when the 'elastic gels' that had been described by Flumiani in 19289 were developed by Semon of the B. F. Goodrich Company^{10,11} into commercially useful plasticised polyvinyl chloride (PVC) in the U.S.A. with parallel, or slightly later, development along the same lines in Germany. The early commercial development in the U.S.A. has been informally described by Davidson, Vice-President of the Union Carbide & Carbon Corporation 12, and the German work has been summarised by Kaufman¹³ in his History of PVC. The old rubber machines, with minor modifications, were capable of working the new materials; however, because of their mechanical deficiencies and inability to maintain accurately the higher temperatures involved, they proved unable to hold the close tolerances on sheet thickness and to maintain the high rates of production soon demanded as an economic necessity by the trade. A long series of engineering developments relating to calenders for the paper and textile trades, typified by Linton's patent¹⁴ of 1901 for in situ roll grinding and Kleinewefers patent¹⁵ of 1905 on minimising roll deflections in embossing machines, were drawn upon by the major rubber and paper machinery manufacturers. Consequently, by 1943, the Troester Company¹⁶ in Germany had produced a calender specifically for vinyl plastics which featured separate d.c. motor drives and gear boxes to each roll, power-operated nip adjustment and cross-axis setting, flood lubrication, and which was capable of operating at temperatures around 200°C. These technicalities are features of present-day machines and are described in Chapter 4. The central problem in the developments of the 1930s, indeed a problem which is still with us, is that of gauge control of thin sheet. The cambering, or crowning, of rolls to compensate for their deflections under load was known to the rubber trade at the time but, by itself, could not solve the problem. The firm of Eck and Son, in Germany, borrowed the principle of cross-axis roll setting from the paper and board industry and applied it to their plastics calender but without the facility of adjustment whilst running and without means for avoiding back-lash in the setting mechanism. Their licensees, the Troester Company, were rather more successful in applying this device in the machine already described. The German machines mentioned were all vertical stack calenders.

Kullgren, in a review article¹⁷ of 1949, described the U.S.A. situation and provided a record of the other major innovations of the period. In particular, reference was made to (a) the inverted L arrangement of rolls that helped to minimise the mutual interaction of nip thrusts, (b) the use of zero clearance, preloaded taper roller bearings, (c) separate gear stacks linked to the rolls through universal coupling and (d) hydraulic loading cylinders to avoid float and back-lash on the adjustments. On these American machines, by combining crowned rolls with cross-axis working and with the better temperature uniformity achieved by peripheral roll drilling, close (+ 0.0002 in or ~ 0.005 mm) control of gauge could be held for long periods of production at claimed speeds of up to 300 ft/min (~ 90 m/min). According to Brown 18 in the discussion following a paper published in 1953, no British calender at that date known to him contained all the mechanical features so far mentioned and he attributed this to economic factors.

The quest for greater precision in calender operation continued through the 1950s, as is instanced by Whittum's patent ¹⁹ of 1953 with the Farrel Birmingham Company. This patent is concerned with the adjustment of roll profiles by grinding to compensate for temperature variations at their extremities, and with this Company's introduction of the Z arrangement of rolls in order to further simplify the pattern of forces influencing each nip. With the introduction of nip profile adjustment by hydraulic roll bending by the Goodyear Company²⁰ in 1955 this account can be considered to have passed beyond history into current technology and the details will be found in later chapters.

1.4 CONTINUOUS THICKNESS MEASUREMENT

In the early days of rubber calendering, it sufficed to control gauge by weighing the finished rolls of sheet, cross-checking with occasional micrometer measurements. As the production rates increased and the tolerances on dimensions became more precise, the need for continuous gauging devices became apparent. At first it sufficed to make a measurement continuously along one or both edges, and Simpson's patent²¹ with the Dunlop Company in 1936 is a good example of such a device; this involves a number of small wheels running on the sheet and on the supporting roll and linked through levers to an 'electric micrometer'. A host of devices involving various physical principles such as magnetism and capacitor effects have been tried but have suffered the defects either of requiring physical contact with the fragile and fast moving sheet, or of yielding

only relative thickness figures. This situation was reviewed briefly by Brown²² in 1955 in an account which probably marks the general acceptance of radiation gauging in the operation of calenders. This highly significant development enabled the machine operators to scan the profile of the sheet as it came from the machine and thus exploit fully the running adjustment facilities that had already been created by the engineering developments described earlier.

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Raw Material Selection

2.1 BASIC POLYMER

2.1.1 General

In industrial parlance polymers or copolymers used in plastics formulations are frequently termed resins and these form the basis of formulations used in calendering processes. As a polymer is usually the largest component by weight in a formulation, polymer choice is a major factor in determining both ease of processing and the properties of the end-product.

Vinyl chloride polymers may be sub-divided into homopolymers, which are usually, but not exclusively, plasticised to give flexible sheeting, and copolymers more usually used in the production of rigid sheeting. There is, in addition, the possibility that the homopolymers or copolymers may have been prepared by either the

mass, suspension or emulsion techniques.

The determination of molecular weight distribution is the fundamental approach to characterising polymers¹. Such measurements, however, are difficult and time-consuming and are not normally used in calendering practice. Instead, a practical quantity termed K-value may be used which is derived from a single viscosity measurement on a polymer solution of given concentration in a suitable solvent². In the U.K. two alternative solvents, nitrobenzene and cyclohexanone, are in use for this measurement on polyvinyl chloride. Each gives different K-values because the viscosity of the solution depends on the particular solvent employed. Because of this, care must be taken when examining commercial literature to take note of the solvents specified. For example, similar polymers may have a K-value of 65 quoted by one company and 72 by another. Fig. 2.1 illustrates these differences in the measurement of K-value.

2.1.2 Choice of Base Polymers

The processing variables of a PVC resin, such as flow, heat stability and softening point, are strongly influenced by polymerisa-

tion technique, molecular weight distribution and the extent of any copolymerisation. Typical commercially available vinyl chloride polymers and copolymers may have properties as summarised in Table 2.1.

Emulsion polymers generally exhibit lower heat stability, less excellent electrical insulating characteristics, impaired mechanical

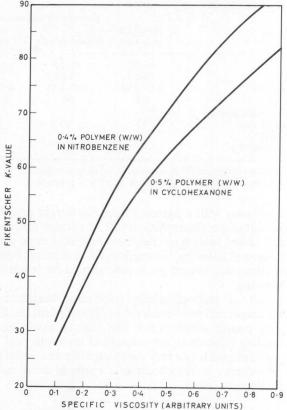


Figure 2.1. Relationship between specific viscosity and Fikentscher K-value

properties and a greater haze when compared to suspension polymers. Their poorer properties are attributable to the presence of residual impurities such as emulsifying agents. However, emulsion polymers may be processed at lower temperatures than suspension polymers and this may confer an advantage in applications where the above properties are not critical. Although copolymers generally exhibit a faster rate of colour development by degradation at a

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given temperature than homopolymers, copolymers containing vinylidene chloride show greater resistance to heat degradation than those containing equivalent amounts of vinyl acetate. Progressive increases in comonomer contents result in reduced heat stability, lower softening point and, with vinyl acetate, lower specific gravity.

Table 2.1 SUMMARY OF PROPERTIES OF TYPICAL PVC POLYMERS

	Emulsion polymers	Granular or suspension polymers	
Property		Homopolymers	Copolymers
K-value (A)	65–55	65–55	65–55
K-value (B)	70-60	72-60	70-55
Bulk density (g/cm ³)	0.47-0.52	0.47-0.55	0.51-0.56
Specific gravity	1.4	1.4	1.4-1.36
Percentage by weight passing			1 1 1 50
B.S.60-mesh screen	99	99	99
Acetate content (%)		0	2–15
Vinylidene content (%)	N - 1	0	4-6

(A) Derived from viscosity of 0.5% solution (w/w) in cyclohexanone

(B) Derived from viscosity of 0.4% solution (w/w) in nitrobenzene.

The use of resins with a narrow molecular weight distribution in blends with other polymers may result in surface defects such as 'nibs' (small raised lumps) or 'fish eyes' (raised lumps surrounded by a rough area of sheeting). Consequently, it is recommended that if different resins are mixed, great care should be taken to ensure efficient blending.

Another set of technologically important variables are the dimensions, shapes and porosities of the polymer particles. The nature of a polymer premix which is not free flowing would give rise to greater handling difficulties. Adjustment of these physical variables results in the availability of a very wide range of commercial polymers and care is required in the choice of a material most suited for a given application.

2.2 PLASTICISERS

2.2.1 General

Plasticisers are generally chemically stable liquids of low vapour pressure, having negligible odour, colour and toxicity and possessing a solvent action on particular polymers. The result of their inclusion is a softening of the polymer. In general, plasticisers may be differentiated from solvents by their much greater molecular weight. In the case of PVC, acetone, with a molecular weight of 58, is a solvent whereas dioctyl phthalate, with a molecular weight of 390, is a plasticiser.

2.2.2 Choice of Plasticisers

The large number of plasticisers available for PVC necessitates some scheme of categorisation. A scheme which is generally accepted and proves useful involves the division of all commercial plasticisers into three main groups in terms of their compatibility with PVC when used individually. Primary plasticisers are those compatible up to the extent of 150 parts plasticiser per 100 parts polymer. Secondary plasticisers, although possessing low compatibility when used alone, exhibit satisfactory solvent power when used in plasticiser blends or where their limit of compatibility is not exceeded. Those materials possessing little or no direct compatibility with PVC are termed plasticiser extenders (or tertiary plasticisers). These latter materials require to be blended with primary plasticisers for incorporation into the plastics mix. In the art it is also quite usual to further sub-divide secondary plasticisers by molecular weight into monomeric plasticisers, which are esters of alcohols and acids whose functionalities do not permit polymer formation, and polymeric plasticisers, which are esters of polyfunctional acids and glycols where limited polymerisation can take place.

Table 2.2 summarises many of the commercially available plasticisers in these three classes; it is by no means a complete list

of the plasticisers that are available.

Present tendencies in plasticiser synthesis veer towards the production of plasticisers for specialised applications. Examples of these include materials with improved heat stability for use in electrical insulation at high temperatures, and plasticisers resistant to oil extraction but which retain flexibility at low temperatures.

Whereas flexible PVC formulations contain plasticiser as a major constituent (i.e., in excess of 25%) with considerable influence on the properties of the compounds, rigid PVC sheeting contains little or no plasticiser. Plasticiser may be included in a rigid formulation to aid pigment dispersion or to improve processing characteristics: but deleterious effects can result from such small inclusions, particularly with copolymers. For example, the plasticiser content should not exceed 2% in vinylidene chloride/vinyl chloride copolymer containing 4% vinylidene chloride because poor impact strength and increased brittleness would result.