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COMBUSTIBLE CARTRIDGE CASES AN ACCOUNT OF THE CURRENT
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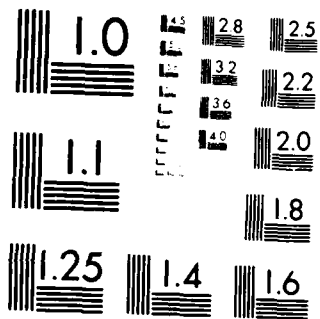
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TECHNICAL REPORT
WSRL-0471-TR

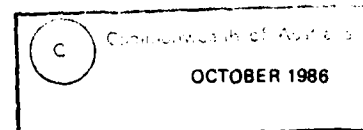
COMBUSTIBLE CARTRIDGE CASES
AN ACCOUNT OF THE CURRENT TECHNOLOGY AND PROPOSALS
FOR FUTURE DEVELOPMENT

V.P. PURI

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TECHNICAL REPORT

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COMBUSTIBLE CARTRIDGE CASES

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FOR FUTURE DEVELOPMENT

V.P. Puri

S U M M A R Y

Combustible cartridge cases are at present produced either by the beater additive or by the post impregnation process. The literature covering these techniques, which basically follow the concept of fibre moulding and/or papermaking, is reviewed. The various processing steps used in the manufacture of these cases, namely, beating, fibre felting and moulding, and resin application are discussed. Particular attention is given to characterising the potential problems associated with the production and use of combustible cases. These include inherent lack of mechanical strength, low porosity, vulnerability to penetration of water and water vapour, and problems related to materials used for fabrication, and complete combustion. In this context, the general areas requiring further research are indicated.



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1. INTRODUCTION

Gun ammunition usually consists of a metal cartridge case, propellant and a projectile in small calibre guns, and a bagged propellant charge with separate projectile in large calibre guns. It is now becoming increasingly common to replace the metal cartridge case or bag with a combustible cartridge case. Various types of combustible objects have been recently used which include combustible cartridge cases, caseless ammunition, combustible detonator holding tubes, combustible rocket fins etc. Combustible cartridge cases, however, are the best known.

Compared to metal cases, combustible cartridge cases are cheap to produce(ref.1), more adaptable to automatic loading, as they eliminate the need to eject the solid parts after firing, supplement the energy of the propellant and lower wear and erosion of the tube. However, these materials lack the mechanical properties exhibited by the metal cases and are therefore more susceptible to environmental deterioration and damage due to rough handling(ref.2).

Bagged propelling charges are currently used in 155 mm Howitzers and other large calibre systems. These charges have presented a variety of problems since their inception generally associated with the use of cloth which, by its very nature, lacks rigidity and dimensional stability. Combustible cartridge cases are an ideal substitute as they offer benefits such as

- improved rigidity and dimensional stability,
- controlled alignment between primer and ignition system,
- automated loading,
- improved ballistic properties, and
- reduction in barrel wear and erosion

Combustible cartridge cases are manufactured from a mixture of energetic nitrocellulose fibres and inert cellulose fibres. Additives, such as polymeric wet strength resins, fillers, waxes and other chemicals are used to improve mechanical strength, performance and other desirable functional properties. As nitrocellulose, the major ingredient used in the manufacture of combustible cartridge cases, is a highly sensitive combustible, safety becomes more important than in metal manufacturing operations. In general, the advantages of using these products outweigh the disadvantages.

1.1 Background

The terms 'consumable' and 'combustible' are used in the literature. The term 'consumable' is applied to the type of ordnance consisting of inert materials only, which are gasified by the heat of the burning propellant. 'Combustible' materials however, contain oxidisers which are capable of providing additional energy.

Consumable ordnance is largely produced using inert cellulosic materials, while incorporation of nitrocellulose, a strong oxidiser, results in a 'combustible' product. At present the emphasis is more on the development of 'combustible' products. The current technology used for the manufacture of combustible cartridge cases is basically adopted from slurry preform and pressing techniques. Earlier investigations(ref.3) were focussed towards developing techniques which involved.

- direct nitration of textiles, nonwoven rayon fabric such as Miracloth, cotton gauze etc, and
- impregnation of nitrated textiles with wet strength resins.

The nitrated cellulosic fabric was laminated by winding around a collapsible mandrel which is rotated under pressure against a rotating internally heated, stainless steel cylinder roll. The fabric sheets were moistened with solvents like diisobutyl ketone, ethylacetate, cyclohexanone, butyl acetate, methyl ethyl ketone, nitrobenzene etc in order to increase the strength of the laminate bond. This laminating technique largely forms the basis of the modern 'wrapping process'.

Later, Beal and Nielsen(ref.4) used a 'felting' technique for making combustible cartridge cases. This involved:

- making up an aqueous slurry of cellulosic fibres,
- forming fibres from the slurry into a mat or a preform of desired dimensions (felting step),
- moulding the preform into the final shape at an elevated temperature, and
- finally nitration of the moulded product using vapour phase nitration with nitrogen pentoxide to a nitrogen content of 13.4%.

These methods caused hazards both in manufacturing and handling, mainly because of the highly sensitive nature of the end products and were not acceptable to industry. Efforts were then made to improve the safety aspects of the already known methods. Recent studies have used techniques based on:

- (a) the formation of nitrocellulose paper and its conversion to a product of a desired specification using spiral wrapping and bonding, or
- (b) the moulding of felted cellulose - nitrocellulose fibres to produce desired end products.

On the basis of resin application two different processes can now be identified in the literature

- (a) Beater Additive Process.
- (b) Post Impregnation Process.

Combustible cartridge cases with acceptable combustion and mechanical properties have been successfully prepared using these techniques in combination with either the wrapping or moulding process(ref.5). The primary aim of any of these processes is to produce combustible cases which maintain the stability, strength and ballistic properties of the combustible material. Current studies are largely directed towards further improving these properties. For example, attempts have been made to improve moisture sensitivity by incorporating water resistant polymer coatings, waxes and also through surface treatments(ref.6). Similarly, products with improved heat resistance have been prepared by coating the walls of the case with a liquid varnish prepared from nitrated polymers(ref.7). Recent comparisons of the beater additive and post-impregnation processes have indicated that the beater additive technique coupled with moulding or spiral wrapping provides generally superior products.

The processing of kraft and nitrocellulose fibres into combustible cartridge cases involve a number of steps which are schematically represented in figures 1 to 3.

2. DESCRIPTION OF THE UNIT PROCESSES INVOLVED IN THE PREPARATION OF COMBUSTIBLE CARTRIDGE CASES

The unit processes involved in the preparation of combustible cartridge cases are:

- 2.1 Stock Preparation
- 2.2 Beater Additions
- 2.3 Pulp Moulding
- 2.4 Paper Formation
- 2.5 Post Impregnation
- 2.6 Spiral Wrapping and Bonding

2.1 Stock Preparation

Stock preparation involves two steps:

- (a) Selection and mixing of fibres, and
- (b) Beating or refining of fibres

2.1.1 Selection and mixing of fibres

Origin, chemical composition and physical characteristics of the NC and cellulose fibres are of great importance in order to prepare the fibre based end product with desirable properties. Some of the important characteristics are:

- (i) Fibre dimensions: Fibre length, fibre thickness, and width of the fibres contribute greatly towards the strength properties of the fibres. For example, tearing strength is directly related to the fibre length. Fibre coarseness is also detrimental in this context.
- (ii) Lignin Content: The quantity of lignin in the fibres is expected to decrease the possibilities of interfibre bonding.
- (iii) Hemicelluloses: These noncellulosic components of wood fibres swell in water, render more flexibility to the fibres, increase the area of interfibre contact and result in partial improvement in interfibre bonding and hence the strength properties of the products.
- (iv) Cellulose: This is considered the backbone of the paper, and is believed to be largely responsible for imparting mechanical strength to the end products.

In general, the strength properties of any fibre-based product depend on the morphological, physical, and chemical nature of the raw material. Fibre length and wall thickness, fragmentation or weakening of the fibres and microfibrils, the degree of polymerisation (DP) of the cellulose, degree of crystallinity and degree of orientation of cellulose are important properties and are usually taken into account during selection and mixing step.

Mixing of various types of fibres is done in order to produce an end product with desirable mechanical and functional properties. During mixing, fibres are suspended in water at 2 to 3% consistency and pumped from the mixing tank to the beater.

2.1.2 Beating of fibres

Beating or refining of fibres is an effective way to:

- enhance fibrillation
- increase total surface or contact area
- impart flexibility to the fibres and
- to obtain a calculated fragmentation of long fibres.

The most commonly employed laboratory or industrial beaters are:

- (i) Holland beaters
- (ii) Valley beaters
- (iii) Conical refiners
- (iv) Lampen mill and
- (v) PFI mill

The pulp fibres are exposed during beating to shear forces as the pulp suspension in water is forced between the bars of the beater. Beating can be influenced by the speed of rotation, design of the beater bar, and pulp consistency. The mechanism of beating is discussed below.

Mechanism of Beating: A dried sheet of unbeaten pulp has comparatively low mechanical strength. The beating process ie mechanical treatment of fibres suspended in water, modifies the fibres in such a way, that an improvement in mechanical strength properties is obtained. The technique, though a very simple mechanical operation, has attracted an immense amount of interest. A number of theories have been advanced to explain the beating mechanism in relation to strength development of the fibres. The most acceptable explanation(ref.11) which has been widely accepted, suggests that the strength development is not solely derived from entanglement of fibres and fibrils, but that the main interfibre cohesion arises from hydrogen bonds developed between the hydroxyl groups of the carbohydrates on adjoining fibres. The process of beating through shearing or frictional forces increases the area of contact between the fibres. For the fibres to weave a network of H-bonds, a very close contact between fibres is desirable, considering the distance between the two 'O' atoms of a hydrogen bond is only of the order of 2.7 to 2.9Å°. In a wet web the fibres are held together by H-bonding through water bridges. Presumably the water in the fibre capillaries maintains dilation of the fibre wall and may reduce interchain associations through a cellulose-HOH-cellulose hydrogen bonding arrangement. Drying, however would draw fibres and microfibrils into close contact, resulting in the formation of stronger interfibre and interfibril hydrogen bonding, and collapse of the lumen(ref.13). These effects, in turn, result in an enhancement of mechanical properties.

As an increment in surface area is an essential criterion for hydrogen bonding, any mechanical treatment need to be carried out in an

environment that facilitates swelling of the fibres and imbibition of the liquid. Water, being polar, and particularly in alkaline conditions, is the preferred medium.

The beating of fibres needs to be closely monitored, since it can also result in mechanical deformation of the fibres, particularly softwood fibres. An ideal beating action is considered to be the one which maximises fibre flexibility and fibre surface area with a minimum of fibre cutting. The properties largely affected by beating, are tensile and burst strength, which show an increase with the increase in interfibre bonding. Tearing strength on the other hand applies a stress of local character, and is a function of the total fibre length.

The overall strength of any fibrous product not only depends upon the strength of the joints between the structural elements, but the strength of these structural elements themselves. The strength of the individual fibres is thus definitely a contributory factor. The strength of fibres varies not only from wood species to species, but also from fibres of the same tree.

2.2 Beater additions

The beating or refining of the fibres is carried out until a desired freeness is obtained. In a beater-additive process (figure 2), resin binders are introduced into the slurry at this point. The resins are precipitated onto the fibres by the addition of cationic agents, thus ensuring that the resin is distributed evenly after felting. Additions of nitrocellulose stabilisers, fillers etc are also made at this point. It is this step which gives the process its name, beater additive. After ageing for a reasonable time (approximately 24 h), the slurry is then moved to a storage tank, where the pulp consistency is lowered to approximately 0.15% solids, and then supplied to either:

- (a) a felting tank which supplies material for a moulding process or
- (b) a distribution tank which supplies material for paper manufacturing.

2.3 Pulp moulding

Pulp moulds are produced by filtering fibres through a screen and felt. The shape and size of the screen and felt determines the shape of the article being made.

The moulding methods can be divided into three categories:

- (i) Soft mouldings, which are oven dried eg plates, egg trays etc.
- (ii) Hard mouldings, which are dried in heated dies eg helmets, textile cones, cabinet backs etc.
- (iii) Full mouldings, which are impregnated with resin and remoulded at high pressure.

Pulp moulding is an ancient technology which dates back to 1700. True pulp moulding however started sometime between 1840 to 1890. The first patent was issued to French and Frost (1856)(ref.14) for equipment by which seamless boxes could be made directly from fibre slurries. Later, a series of patents were issued (1866-1900), which covered the area related to equipment for felting preform, presses to remove excess water and equipment for drying the moulds(ref.15,16). An automatic felting equipment was

developed by Keyes in 1903(ref.17). Manson(ref.18) and Chaplin(ref.19) (1928) were credited for the development of die-dyeing process. This technique was later successfully automated by Pellegrino and co-workers(ref.20) in 1964. In the last twenty years moulding technology has undergone tremendous changes, and the present state-of-the-art seems very close to its full potential. However, if the demand of moulded products continues to grow, it is expected that the future technology, even though it will be largely based on current state-of-the-art practices, will definitely be more efficient and effective.

2.3.1 Stock distribution and felting

Metered amounts of fibre slurry from the storage tank are dropped into the felting tank. The excess water is removed using vacuum. The moulding die which rests on the felting tank platform can be easily moved in and out of the slurry. The preform from the die is taken away using compressed air. The overall weight of the felted preform is critical in pulp moulding and is controlled by the freeness of the stock, pulp consistency, vacuum applied and the time used for felting.

The preform contains approximately 70 to 75% water as it is felted. The wet strength of the preform is directly related to the quantity of water held by the fibres at preform stage. Presumably, the higher the water content, the lower is the wet strength. The measurement of 'wet web strength' at this stage is essential to ascertain the strength of the fibres at a given water content, as this is useful in designing the parameters required to form a mould of desired properties.

Felting is a filtration process, where fibres from the dilute solutions are deposited onto the felt. The fibres are held together through H-bonding. The time when the mould or preform comes out of the felting tank is a critical point, and the wet web strength of the fibres plays an important role. Also, the losses in the white water are important. These include "fines" which are produced by the beating and cutting action of the fibres in the beater. In a beater additive process, a considerable amount of wet strength resin is also lost. Recirculation of white water into the felting tank is considered useful in reducing loss of fines and resin.

2.3.2 Drying of the preform

The wet preform contains approximately 70 to 75% water. The excess water is removed by placing the wet preform in heated and vented dies under pressure and vacuum. It is desirable to use pressure felting technique, where water content in the preform can be reduced to about 50%. At this moisture level the felt is relatively dry and does not elongate. This ensures that the problems related to edge moulding do not occur. Heat and pressure used in the moulding operation is generally sufficient to cure the resin.

2.4 Paper manufacture

Alternatively, the slurry from the distribution tank is supplied to the paper making machine, where it undergoes fibre distribution, removal of excess water through pressure filtering techniques and finally passes through heated cylinder rolls. The paper is used for conversion to combustible cases of desired dimensions by using spiral wrapping and bonding techniques.

2.5 Post impregnation

An alternative to the beater additive process, is to immerse the moulded and dried preform or paper in a resin solution in order to modify the functional and mechanical properties of the product. This process is called the post impregnation process (figure 3).

The earliest known coating compositions were largely based on spirit varnishes. Nitrocellulose based coatings were popular in the early 1920's. Other cellulose derivatives such as cellulose acetate, ethyl cellulose and mixed cellulose esters, and synthetic resins were used in large quantities. These coatings were used to provide:

- resistance to water, and water vapour,
- resistance to chemicals, drugs and foods,
- physical resistance to scuffing,
- resistance to abrasion and folding, and
- heat sealing properties.

It is desirable that the coatings should be

- free from odour, taste and toxicity,
- resistance to discolouration by sunlight,
- of reasonable cost,
- able to provide good adhesion to the base,
- inflammable,
- stable to ageing
- non-blocking under reasonable pressure and temperature

The literature reveals that it is extremely difficult to develop a coating system which exhibited all the desired properties. However, some of the properties are indispensable for any conceivable use. For example, unless the coating has good adhesion, its value is limited. The formulations for coating compositions are designed to maximize the properties most desired.

2.5.1 Application techniques

The most commonly employed techniques are:

- doctor knife coating (widely used)
- roll coating (widely used)
- spray coating
- air brush coating

2.5.2 Composition of solvent coating solutions

The solvent based coating compositions usually constitute:

- (i) Primary film forming materials
- (ii) Secondary film forming materials
- (iii) Plasticisers
- (iv) Pigments, dyes, fillers etc.

The principal binding component of any coating compositions comes from primary film forming materials. Secondary film forming materials are used to modify the properties of the primary film forming material. Properties such as solubility, resin compatibility, and plasticizer compatibility are considered important in order to obtain uniform coatings.

2.5.3 Solvent systems

Volatile organic solvents are generally used. Esters, alcohols, ketones, aliphatic and aromatic hydrocarbons are by far the most common solvents used in the paper and fibre coating field. Selection of a solvent is based on its solvency properties, viscosity, concentration, evaporation rate, odour, toxicity, flash point and explosive limits, cost and ease of recovery.

2.5.4 Effect of solvents on film properties

The primary function of any solvent mixture is to alter the physical state of the coating material, so that it could be applied uniformly to the desired surface. The solvent must be also easy to remove. Commonly experienced problems related to solvent coatings are:

Specks: These are formed during improper filtration of the coating solution.

Scratches: This problem mainly occurs when the knife coating technique is used, as accumulation of particles causes scratching of the materials.

Bubbles: These are usually formed during the rapid drying of the solvent or result from pinholes in the paper.

Peel: This can result from poor solvent balance or too rapid drying.

Blushing: Results from the condensation of moisture from the air, or precipitation of part of the nonvolatiles during solvent imbalance.

Curling: Mainly occurs owing to insufficient plasticiser, resulting in excessive shrinking on drying.

Blocking: This is caused by the tackiness resulting from either solvent retention, or from an over plasticized film.

2.6 Spiral wrapping

The moulding of fibres into desirable configuration is a useful process, but it is not very efficient. To increase the overall efficiency, efforts have been made to convert the nitrocellulose based combustible paper to

combustible cases using a continuous process by the winding technique. Standard commercial paper-making equipment is used to manufacture nitrocellulose paper rolls. These rolls are placed in a commercial spiral core-winding machine. These machines are capable of producing tubing in a variety of diameters, lengths and laminates.

It should, however, be realised that spiral wrapping techniques can only be used to fabricate case sidewalls. Additional components like caps, igniter caps, glue rings etc can only be produced by conventional fibre moulding techniques.

3. HAZARDS AND ECONOMICS

3.1 Hazards

The important considerations, particularly in the use of solvent coating systems, are:

- fire
- explosion and
- toxicity

The majority of the organic solvents used in solvent coating compositions are highly inflammable. These solvents are capable of forming explosive mixtures with air within certain ranges of concentration. Fire and explosion, therefore, are the two major hazards which need to be guarded against during all phases of manufacture. Additional care is required in the handling and use of nitrocellulose based products as drying renders these products more susceptible to fire. Also many of the commonly used solvents can be toxic and proper ventilation is highly desirable.

3.2 Economics

It is important to compare the costs involved in solvent or aqueous coatings. Obviously, solvent based coatings cost more than beater addition techniques. The overall cost resulting from the post impregnation process depends on factors such as: cost of material, film thickness or total solids in the coating composition, and application techniques.

However, if there are certain characteristics which can only be achieved using a solvent coating system, then a properly designed and efficiently operated system can dramatically reduce the cost. Also, if the amount of solvent used is sufficiently large, a solvent recovery system can effectively lower the overall cost. In general, solvent coatings are more expensive and more hazardous compared to beater addition and aqueous coating systems.

4. CURRENT STATUS

The current intense interest in the utilization of combustible cartridge cases for mortar containers, artillery propellant charges, tank rocket systems and small calibre ammunition has prompted many studies on the improvement and/or development of these products. It has been acknowledged that the beater additive technology is superior to the post impregnation technology, when safety and cost factor are taken into account. However, the currently available beater additive resins do not produce as good a product as the

solvent resin system. Both technologies are almost equally being used at present, as reflected in the type of products either in production or the development stage (Table 1)(ref.21).

The beater additive moulding technique, which is the preferred technique at present, is ideal for small scale production. If the consumer demand continues with the present rate, it would be necessary to use automated manufacturing techniques comparable to paper manufacturing methods, so as to reduce manufacturing cost while improving product quality. In this context, the beater additive - spiral wrapping process is being currently studied widely. If it proves to be commercially viable, this offers the flexibility for tailoring the laminations of the case in such a way that the energy capacity of outer and inner layers can be altered to improve combustion and ballistic properties.

5. FUTURE OBJECTIVES

Regardless of the present state of the technology and our present knowledge of the individual components used in the manufacture of combustible cartridge cases, there is still a significant gap in our basic knowledge of the subject. Future studies, which should facilitate the task of devising suitable methods for the production of combustible cases, should consider the following:

- (i) An overall improvement in the physical strength of the product.
- (ii) Development and/or assessment of polymeric resins to improve mechanical and functional properties.
- (iii) Replacement of nitrocellulose, a highly sensitive material, with other energetic synthetic organic compounds.
- (iv) Development of compositions which could make use of injection moulding or extruding technology, in order to improve manufacturing efficiencies, density, structural strength and combustibility characteristics.
- (v) Development of a process which is fully automated, quicker and results in the safe production of the combustible materials.

6. SUGGESTED RESEARCH STRATEGIES

6.1 Problem areas

A number of reports appearing in the literature in the past ten years (ref.5,8,22 to 24) covered various aspects of combustible case technology. These include problems related to materials used in preparation, design, manufacture and performance of these products. However, it is extremely difficult from the results presently available, to conclusively answer some of the fundamental questions such as:

- (i) Is it essential to use uniformly nitrated fibres, as has been previously suggested?
- (ii) Does the initial degree of polymerization of cellulose, perhaps through its influence on other structural factors, play a significant role in the rate and extent of nitration, and hence the performance of the product?

(iii) Does the crystallinity, crystallite size and dimensions of the micelles directly affect the nitration or the physical properties of the end product?

(iv) Does the variation in nitrogen content of cellulose affect the mechanical performance of the cartridge cases?

(v) What is the actual role of kraft fibres in the composition? Is it solely for providing a gain in physical strength, or does it affect the overall performance of the product?

(vi) Is the incomplete burning and moisture sensitivity, experienced so widely, in any way related to the use of pulp fibres?

(vii) Is it possible to replace kraft fibres with synthetic fibres in order to improve tearing resistance?

(viii) Is it possible to improve overall physical characteristics by the application of cross-linking agents or organometallic chelating agents?

Since literature does not provide unequivocal answers to these and many other related questions, it is necessary to undertake research to clarify our basic understanding of the mechanisms involved in the production of the combustible cartridge cases. It is only through an improved understanding of these problem areas that a superior product will be produced.

6.2 Proposed research options

6.2.1 Wood pulp vs cotton linters

It has been invariably suggested that the nitrocellulose produced from cotton linters exhibits superior properties (particularly in explosives formulations) compared to nitrocellulose derived from wood cellulose. Morphologically, these materials differ markedly, in particular, fibre length, fibre uniformity, D.P., degree of crystallinity etc. It has been suggested(ref.25) that wood pulps contain appreciable amount of short fibres, which on nitration yield lower degree of substitution. The resultant nitrocellulose is less soluble and contains a high amount of gels. Presumably, the physical properties of a product containing these components may show some variation. Whether the effect is detrimental, when these materials are used for the preparation of combustible cases, needs to be investigated. It is rather difficult from the result presently available to isolate such structural features which could readily explain the behaviour of the end product.

It has been revealed that there is a definite correlation of microscopic structure of cellulose to its macroscopic properties(ref.26). Prask and Choi(ref.27) extended this concept to nitrocellulose prepared from kraft, sulphite pulps, and cotton linters, and mainly concentrated on defining the crystalline nature of the materials and their effect on the properties. The study however, failed to account for the various characteristics of cellulose, such as D.P., surface area, fibre length etc, and their relation to nitrocellulose. There is a need to specifically determine the effect of structural features of cellulose derived from various sources, on the nitrated samples and to the products manufactured thereof. The studies should clarify the effect of varying degrees of substitution during nitration on the overall crystallinity, dimensions of crystallinity and micelles, its relationship to strength properties, behaviour in energetic formulations, and changes that may occur on exposure to varying degrees of temperature and humidity.

6.2.2 Beater additives

The polymeric synthetic resins are usually employed as beater additives. These resins produce materials which are rigid and very brittle. As the resins tend to coat the fibres almost completely, it greatly reduces the fibre to fibre bonding. The overall strength of the dried and cured paper, or a mould, largely depends on the properties of the resin used. In order to maximise the strength properties, it would be desirable to tap certain inherent characteristics of the materials used. Studies should be directed to assess the affect of various resins on strength properties or alternatively the use of grafted cellulose fibres should be explored in this context. It may be desirable to use high strength polyfunctional grafted cellulosic compositions, which could result in an increase in mechanical and functional properties.

A considerable quantity of resin is lost in the white water foaming. This causes problems of drainage and fouling of the equipment over a certain period. A systematic study of precipitating agents and processing conditions should be carried out to alleviate this problem.

Alternatively, "in situ" polymerisation either using monomers or prepolymers could be investigated. This technique could effectively introduce desirable functionalities through fibre-polymer interactions.

The primary aim of the resin application is to obtain high mechanical strength. It is also advantageous to employ binders, which result in a composite material which is substantially non-porous and non-permeable. Cross-linked resin systems are thus preferred. To increase the cross-linking it may be useful to introduce crosslinking agents or organometallic chelating agents. This area needs to be fully investigated.

6.2.3 Kraft fibres vs synthetic fibres

Kraft fibres are added to provide physical strength. These fibres are highly susceptible to processing conditions, particularly beating. Overprocessing or overbeating can reduce the fibre length dramatically, resulting in a low tearing resistance. It may be possible to replace the kraft fibre component, either in part or fully, with synthetic fibres which could result in increased mechanical strength and decreased moisture susceptibility. The addition of synthetic fibres may also improve the combustion properties and reduce the overall residue.

6.2.4 Nitrocellulose vs synthetic organic compounds

Nitrocellulose is a highly sensitive material. A significant problem in the use of combustible cases with high nitrocellulose content in automatic weapons having a high rate of fire, is the problem of self ignition of the combustible cases. In these weapons, substantial heating of the internal breech and barrel walls takes place, and the temperatures can reach as high as 250°C, which is above the ignition temperature of the materials used. Varnishes based on nitrated polymers or copolymers have been used to coat the walls of the cases in order to increase the heat resistance characteristics(ref.7).

Also, cellulose and nitrocellulose fibres are very susceptible to water absorption if stored for any appreciable length of time in an atmosphere containing a high degree of moisture. Swelling of the cases or penetration of moisture into explosive stores could create an

environment which is potentially hazardous. In extreme cases, misfiring can occur. This problem has been very well recognised and various measures have been suggested to overcome this problem(ref.6).

These problems highlight the need to either modify these materials to increase heat resistance and water repellency by using polyfunctional resinous binders, or reduce or remove the nitrocellulose and cellulose components. The use of polyvinyl nitrate as part replacement for nitrocellulose has already been suggested(ref.28). It may, therefore, be advantageous to incorporate other nitro-organic polymers in the formulation, which are energetic and exhibit heat resistant and water repellent characteristics. The use of such polymers may allow the use of injection moulding or extrusion technologies which offer increased manufacturing efficiencies, and help improve problems related to density, structural strength and combustibility.

6.2.5 Moulding vs spiral wrapping

The use of a spiral wrapping process is limited at present, mainly because of low mechanical strength of NC paper. This technique in comparison to moulding is fast and allows the introduction of variations in laminates, such as covering of higher and lower energy content inner layers with an outer inert layer. The technique is useful for high volume production, and in the manufacture of combustible cases of any desirable size and dimensions. Application of spiral wrapping may therefore be desirable in future. This provides added incentive for the development of high strength resinous materials which would provide substantial increase in strength of the NC paper.

ACKNOWLEDGEMENTS

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GLOSSARY OF THE TERMS

1. CELLULOSE: A major component of a secondary cell wall, chemically it can be defined as a linear homopolysaccharide of β -D- glucopyranose units linked together by (1 $\rightarrow$ 4) glycosidic bonds.
2. HEMICELLULOSES: The non-cellulose component of wood is called hemicellulose. These are heterocopolysaccharides and function as supporting materials in the cell walls.
3. LIGNIN: Lignin is an aromatic polymer in the wood consisting mainly of phenylpropane units. In chemical terms, lignin can be defined as a dehydrogenation polymer of coniferyl alcohol (gymnosperm lignin), or coniferyl and sinapyl alcohol (Angiosperm lignin), or a mixed dehydrogenation polymer of coniferyl, sinapyl and p-coumaryl alcohols (grass lignin).
4. CONSISTENCY: This is defined as the percentage amount of fibres in a given slurry.
5. FREENESS: This is defined as a measure of the drainage capacity of different pulp types. Depending upon the equipment used it is reported as CSF (Canadian standard freeness) or SR (Schopper Reigler).
6. WHITE WATER: The water drained during moulding or paper making process is referred to as white water. White water usually contains significant amounts of fines and other additives added during the beating process.
7. FINES: The fibrous material produced during beating of the fibres, which is not retained by the felting mesh during the moulding or paper making process.

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TABLE 1. CURRENT PRODUCTS, PRODUCERS AND THE TECHNOLOGY USED(ref.21)

Product	Producer	Process
Combustible Cartridge Cases		
- 120 mm KE and Heat Rounds (Rheinmetal Smooth Bore Gun)	Criton-Armtec, USA SA Les Forges De Zeebrugge (FZ), Belgium	Post Impregnation
	WNC - Nitrochemie, FRG	" "
	SNPE, France	" "
- 120 mm for Chieftain Tank	ROF Bishopton, UK	" "
	WNC - Nitrochemie, FRG	" "
- 155 mm FH70 Charge Con- tainers	ROF Bishopton, UK	Beater Additive
	WNC Nitrochemie, FRG	" "
- 155 mm M109G Howitzer	FZ, Belgium	Post Impregnation
- 155 mm M203E2 Charge Con- tainer	Criton-Armtec, USA	Beater Additive
- 155 mm Case for the GCT Howitzer	SNPE, France	" "
Mortar Propellant Containers		
- 60 mm mortar	Criton - Armtec, USA	Beater Additive
- 81 mm mortar	Criton - Armtec, USA	" "
Igniter Tubes		
- 155 mm M203 Propellant Charge	Criton - Armtec, USA	" "
- 8 inch M188A1 Propellant Charge	" " "	" "

TABLE 1(CONTD.).

PRODUCTS IN DEVELOPMENT

Product	Developer	Process
Combustible Cartridge Cases		
- 90 mm AA and ATK gun	F2, Belgium	Post Impregnation
- US 105 mm Howitzer	" "	" "
- 105 mm gun (Leopard 1)	" "	" "
- 40 mm	WNC - Nitrochemie, FRG	" "
- 155 mm FH70 (Multi Composition Cases)	" "	Beater Additive
- 155 mm various types	SNPE, France	Spiral Wrap
	Criton - Armtec, USA	" "
	Dynamit Novel, FRG	" "
Modular Charges		
- 155 mm various types	SNPE, France	Beater Additive
	Criton - Armtec, USA	" "
	WNC Nitrochemie, FRG	" "
Tubes		
- Primary Boost in Rocket	WNC - Nitrochemie, FRG	Unknown Motors
Mortar Increments		
- 120 mm	Criton - Armtec, USA	Beater Additive

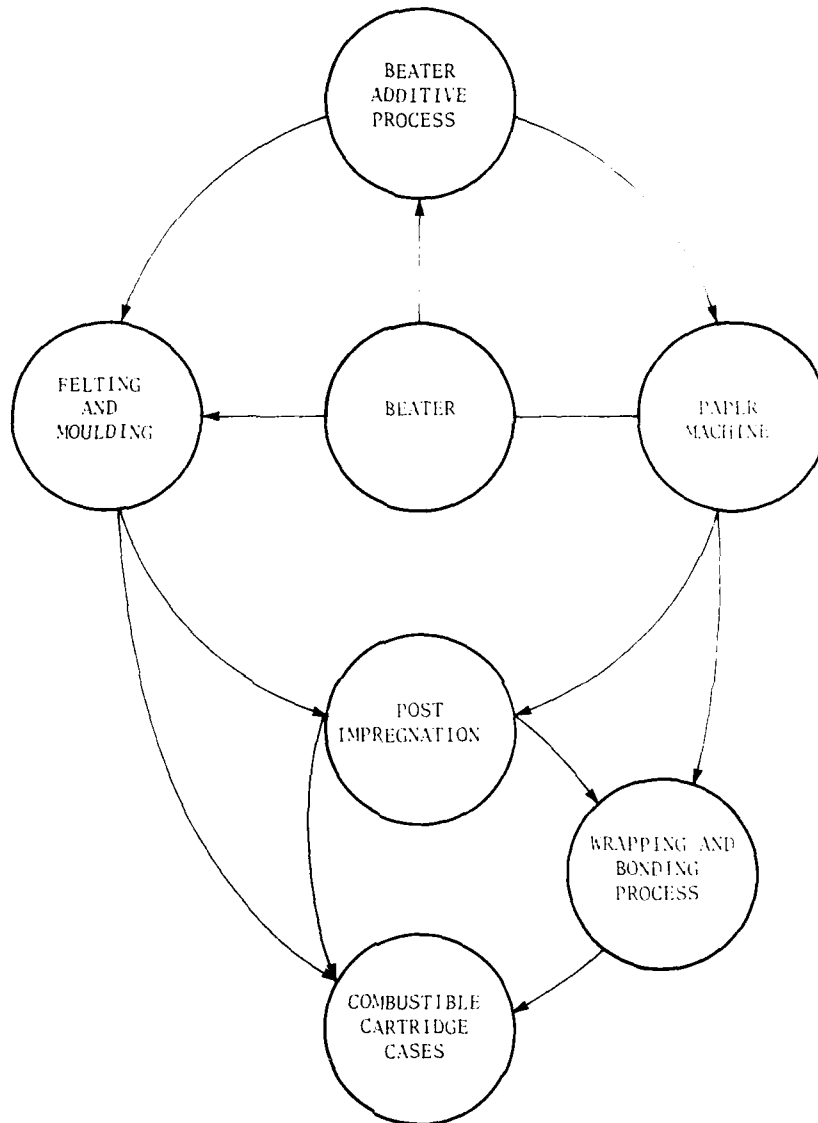


Figure 1. Processing of kraft pulp and NC fibres to combustible cartridge cases

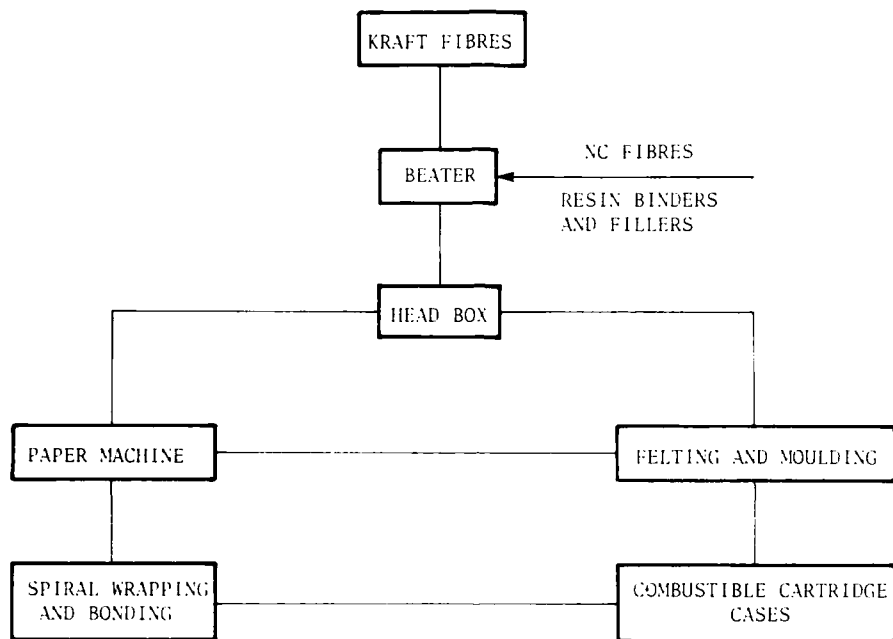


Figure 2. Schematic diagram for the preparation of combustible cartridge cases using the beater-additive technique

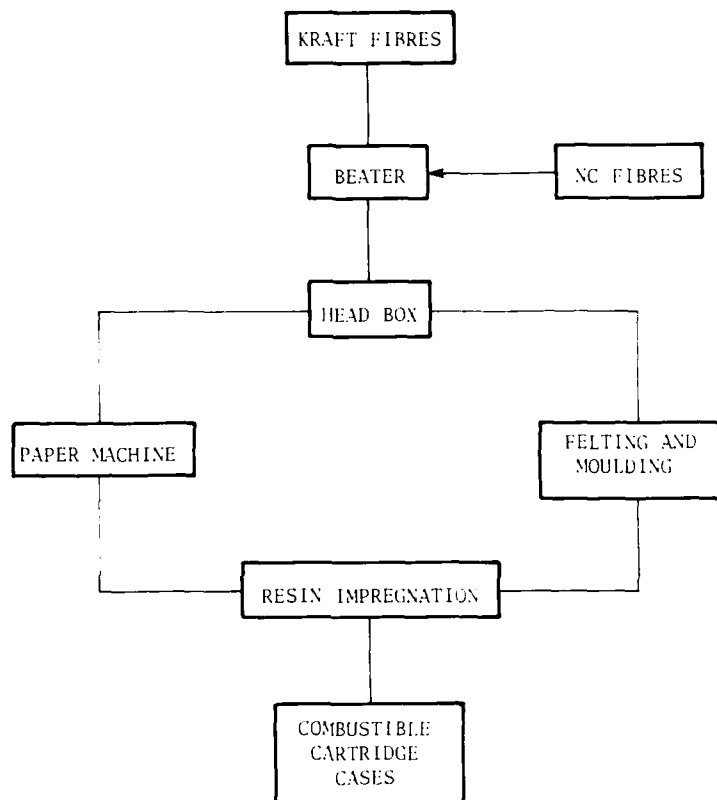


Figure 3. Schematic diagram for the preparation of cartridge cases using the post impregnation technique

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APPENDIX I

KRAFT PROCESS

The term kraft or sulphate is used to describe the process where wood chips are cooked with sodium hydroxide and sodium sulphide under high temperature (170 to 180°C) and pressure (100 psi). Sodium sulphate is used as the make-up chemical to compensate for the losses of sodium sulphide during the recovery cycle of cooking chemical. The sulphate process is named after this process.

The kraft pulping process is a widely used process which is applicable to all wood species for the production of pulp of high strength properties. A simplified version of kraft pulping conditions is given below:

The cooking liquor is predominantly sodium hydroxide and sodium sulphide. The following terms are commonly used in pulping industry.

(i) Active Alkali. The sum of NaOH and Na₂S charged, calculated as sodium equivalents and expressed as Na₂O. This concept implies that the hydrolysis of sulphide proceeds completely to H₂S leaving 2 moles of -OH per mole sulphide available for pulping. But in practice the available pH in the kraft cook does not allow complete hydrolysis and only one mole -OH per mole sulphide is liberated.

(ii) Effective Alkali. The term 'Effective Alkali' is used to represent NaOH + $\frac{1}{2}$ Na₂S, calculated as sodium equivalents expressed as Na₂O.

The amount of active alkali in the cooking liquor ranges from 200 to 225 kg/ton of wood. The liquor to wood ratio is kept at around 3.5:1. The maximum digester temperature ranges from 160 to 180°C with corresponding steam pressures. Cooking times at maximum temperature vary from 1 to 2.5 h.

Wood is mainly composed of three major constituents viz, cellulose, hemicelluloses and lignin. Cellulose and hemicelluloses together (Holocellulose) represent the total carbohydrate components of wood and are desirable for paper making. Lignin, believed to act as a cementing medium, is completely aromatic in nature and is considered undesirable for paper making. The kraft cooking process effectively removes the majority of the lignin, but in the process almost all the hemicelluloses are also dissolved.

The chemicals from the cooking liquor ("Black Liquor") are usually recovered and reused. Flow diagrams showing wood processing and chemical recovery system are given in figures I.1 and I.2.

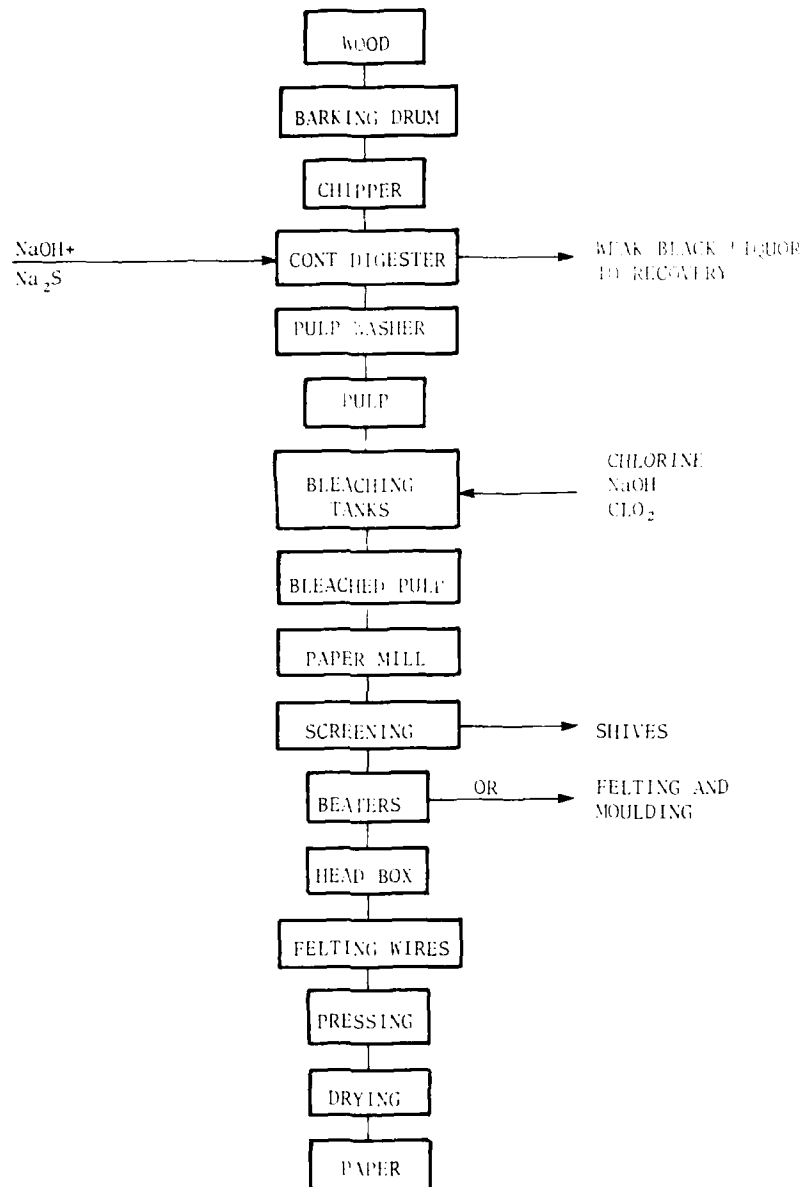


Figure 1.1 Production of paper using the Kraft process

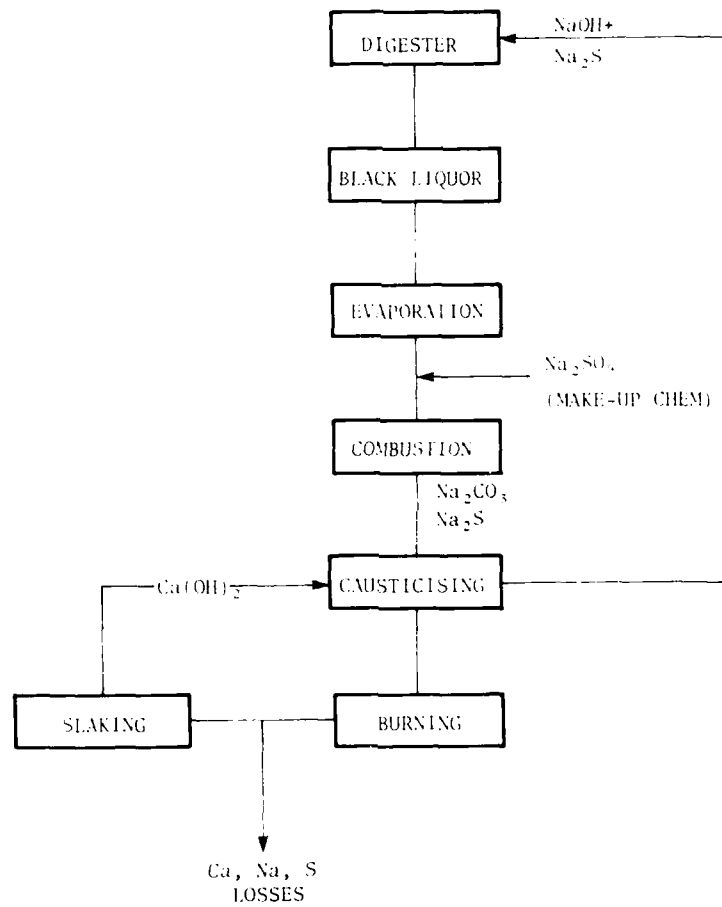


Figure 1.2 Recovery of Kraft chemicals

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Terms

Manufacturing methods

16 SUMMARY OR ABSTRACT

(if this is security classified, the announcement of this report will be similarly classified)

- Combustible cartridge cases are at present produced either by the beater additive or by the post impregnation process. The literature covering these techniques, which basically follow the concept of fibre moulding and/or papermaking, is reviewed. The various processing steps used in the manufacture of these cases, namely, beating, fibre felting and moulding, and resin application are discussed. Particular attention is given to characterising the potential problems associated with the production and use of combustible cases. These include inherent lack of mechanical strength, low porosity, vulnerability to penetration of water and water vapour, and problems related to materials used for fabrication, and complete combustion. In this context, the general areas requiring further research are indicated.

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