Deve'opments in technology : Carbonless copy papers

SAIKIA C. N.* & CHALIHA B. P.*

SUMMARY

The Carbonless Copy Papers are designed to eliminate the carbon interleavers used with the conventional multiple copy system. Because of its assured applications in many fields, the future of CCP seems to be very promising, with a world wide growth rate of 10 percent per year. The present article discusses the development and status of CCP technology and gives in a nutshell a picture of the world scene of the carbonless copy system. The indigenous techno ogy developed is also discussed in brief.

INTRODUCTION

In recent years, one of the most widely expanded and consumer accepted copying papers is the chemical cabonless copy papers. The carbonless copy paper, as in the case of carbon papers, does not use any visible coloured coatings but the system depends mainly on two colourless coated surfaces, one that acts as donor surface and other as receptor or acceptor surface. Chemical reaction occurs when the chemicals of the donor surface come in contact with the chemical present in the receptor surface under the action of heat or pressure, thereby producing a distinctive coloured image. Figure I, represents a carbonless copy paper system

The use of cabon papers have certain limitations due to its functional and aesthetic short comings and other associated factors such as disposal and ecological problems, toxicity etc. More over, carbon paper cannot conveniently be used in modern business machines like electronic data processing equipments and computers because of its increased weight and thickness. Many specialised business forms like credit card forms, airlines tickets, invoice, purchase order forms etc. cannot be made conveniently with carbon interleaver system. The increasing demand for complex business forms and multi part sets and also development of modern business machines are some of the important factors that led to the growth of carbonless copy papers.

There are numerous other advantages to the use of carbonles papers in the business environment. No special machinery or new skills are required for printing of this paper. The readability of copies produced in computer printers with carbonless copy paper is more clear and distinct and is essentially an improvement over one time carbon papers. The images from carbonless copy paper are smudgeless and its quality will not deteriorate with time and repeated handling as is often the

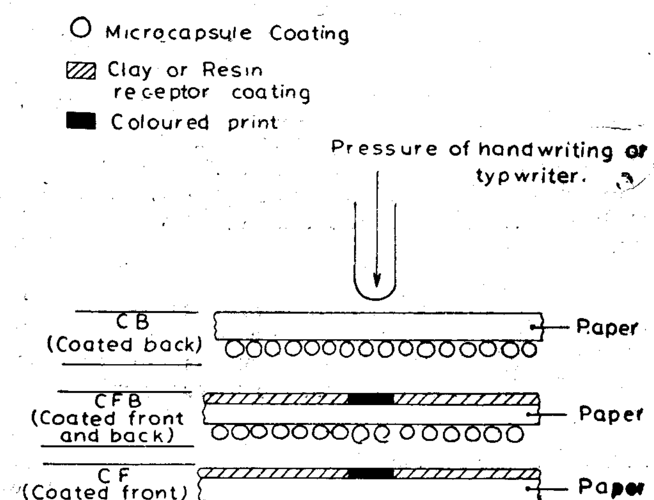


Fig. 1 Carbonless Copy Paper System

*Regional Research.Laboratory, Jorhat-785006

case with one time carbon copies. The image produced from carbonless copy system is also not easily erasible and hence security is another justification for use of this type of paper. An important consideration for user is that the handling and distribution of forms are simplified with carbonless system. The time and cost of removing carbon is eliminated. The carbonless forms can be made immediately ready for separation after printing or typing. Another prime factor for growth of this unique system is its use in modern business machines with three significant results e g. (i) feeding through electronic data processing and handling equipment is improved (ii) the bulk of interleaved sheets is reduced and (iii) double the quantity of paper can be accommodated to feed system[1].

EARLY DEVELOPMENTS :

In the early stage of development of carbonless copy paper, inorganic salts which produce colour on reaction systems, were used for coating on base paper together with suitable binder. The reactive inorganic compounds were coated on both sides of paper. The printing marks on the copy obtained from this system were not sharp and it was also difficult to get instant print marks because most of the inorganic salt combinations do not produce instant colour in dry state. The papers obtained from inorganic salt combinations did not find favour with users. combinations of two colourless components soluble in water are coated separately in emulsion from to produce this type of paper. The result was colouration before applications of pressure[2]. The trend had since been changed to produce coated carbonless copy papers by using some organic dye intermediates. Some leucoderivatives of basic dyes were used for coating on paper together with a binder like starch, methyl cellulose, butyl rubber latex, modified starch etc. But as most of the dyes are fugitive to the sunlight and also undergo atmospheric oxidation, it became quite impossible to keep the dyes in colourless forms. Moreover, the problem of smudging was always there.

The solution to all these problems such as reversion of colour of dyes due to oxidation, smudging and durability of printing marks etc. was achieved by the introduction of the microencapsulation technique.

MICROENCAPSULATION :

Microencapsulation can be best described as a micropackaging technique that deals with 'packaging' of various liquids, solids and gases in ultraminiature containers or capsules, which alter the basic characteristics on application possibilities of a material. Broadly, microencapsulation provides a means of packaging, separating and storing materials on microscopic scale for later release under certain controlled conditions. Minute particles or droplets of almost all materials can be enveloped in a thin, uniform film of polymeric material and thus isolated from reactive. corrosive or hostile atmospheres or surroundings. The conditions of release may depend upon moisture, pH, physical force or combination thereof. The contents of the capsule can be made available by mechanical rupture of the capsule wall, by causing its disintegration by chemical or electrical means or by leaching action carried out in an appropriate liquid environment. Broadly, the release mechanisms may by pressure, temperature, chemical or solvent action and many others.

The technology of microencapsulation is well established. The concept of microcapsules was first developed by De Jong[3]. The structure of microcapsules resembles that of a living tissue, consisting of thin membrane called "wall" surrounding the discrete amount of matter. Their walls may be of wax, natural polymers like gelatine, plastics or metals and thier quantity may vary from 20 percent of the total capsule weight to almost 100 percent. Microcapsules are measured in microns and usually fall into the range of from several to approximately 200 microns.[4]

The first commercial exploitation of microencapsulation technology came with the development of carbonless copy paper, where several methods of microencapsulation are utilised to encapsulate the system of leuco-dyes.

The primary requirement of microcapsules for use in carbonless copy paper is to have size in the range of 1-10 mu. This is needed to prevent premature or accidental rupture of the microcapsules. The capsule wall should be insoluble in the encapsulating material. The film forming material should be non-porous to contain and protect the marking fluid and tough or abrasion resistant to prevent premature rupture due to incidental scuffing. The encapsulated core material should not contain any other reactive or potentially harmful material which may damage the polymeric wall.

The microencapsulation is performed by various processes. One of the best known processes for microencapsulation is the 'coacervation' process, which can be accomplished in two ways—the 'simple or salt' coacervation and 'complex' coacervation. The simple coacervation system is generally not followed for carbonless copy paper. The complex coacervation system is the most widely accepted system which can be accomplished in three distinctive steps[5]. In the first step, the liquid or solid which is to be encapsulated is emulsified or dispersed in a suitable dispersion medium and most frequently, the medium may be a solution of the intended capsule wall material. In the second step, the solvent characteristics of the polymer solutions are changed, such as to cause separation of the mater ial The wall material is also contained in a liquid phase, as the intended capsule content. In the third step, the liquid wall material phase deposits itself as a continuous coating about the dispersed droplets or particles of the internal phase and then the continuous wall of the capsule are hardened before the capsules can be done by one of the number of techniques viz. drying, tanning or polymerising the wall material. Depending on the technique and the process conditions, the wall material can be made more or less porous, harder or tougher. In addition, the agitation of the system during microencapsulation can also affect the thickness of the wall of the capsules. Figure 2 shows the stages in complex coacervation system. Photographs show the different forms of coacervate and microcapsules.

Materials which possess an ionizable group and exhibit electric charge in colloidal solutions are coacervable and are mostly used in the complex coacervation system of microencapsulation. Some kinds of hydrophillic colloid ions in aqueous solution are negatively charged regardless of the pH of the solution while some are positively charged and some are amphoteric having an isoelectric point, above which they are negatively charged and below which they are positively charged[6]. Such materials include natural and synthetic macromolecular species like gelatin, gum-arabic, acacia, tragacanth, agar agar, styrene maleic anhydride copolymers, methylvinylethermaleic anhydride copolymers, polymethacrylic acid and the like, polyvinyl alcohol, methyl cellulose, carboxymethyl cellulose etc.

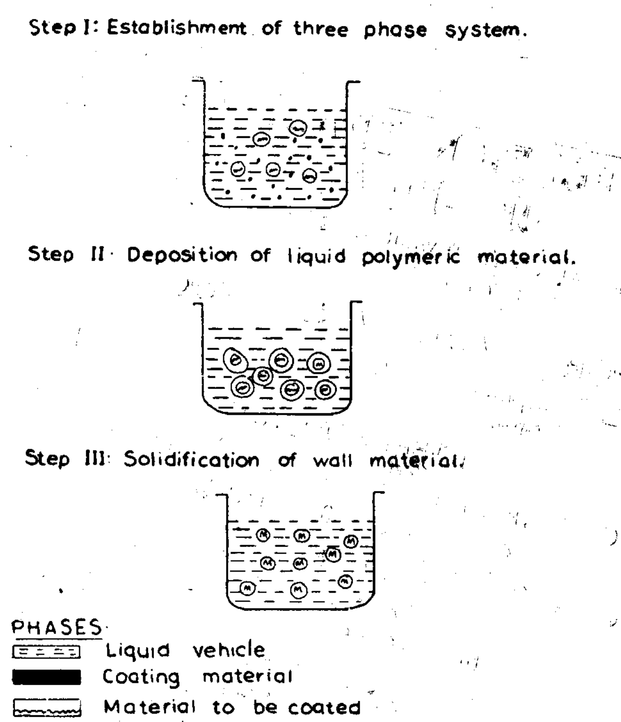
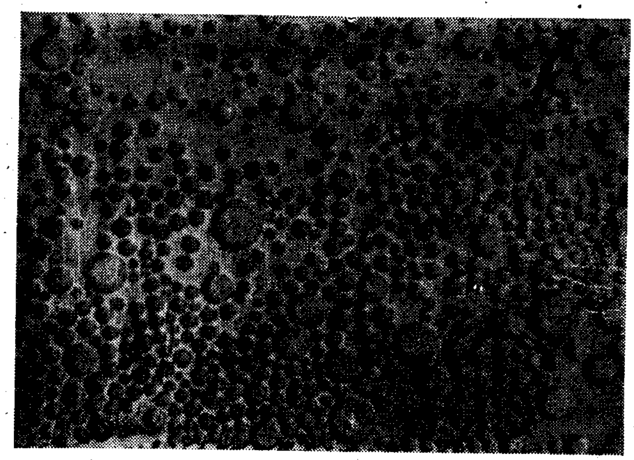
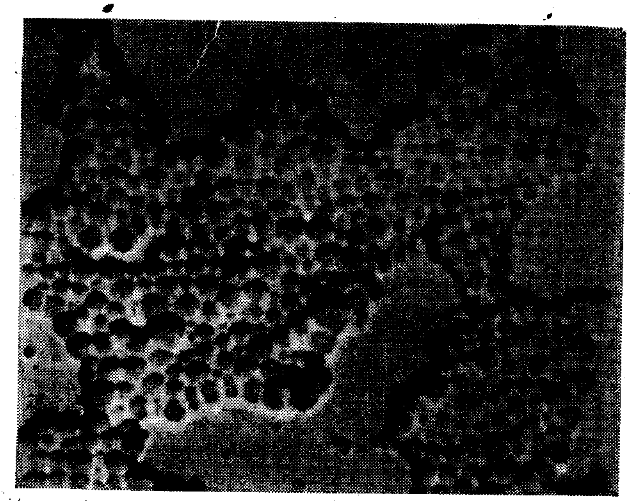


Fig. 2 Different Steps in Coacervation System



Photograph I : Complex Coacervate Droplets of Gelatine Gum Arabic Complex.



Photograph II : Oil Containing Microcapsules.

The traditional methods of producing microcapsules are mostly based on complex coacervation system. Methods are now available for producing microcapsules of oil in water emulsion adopting techniques other than coacervation. In such a process, oil-in-water emulsions can be encapsulated by using hydrophillic and hydrophobic polymers and resins, whereby microcapsules with superior properties can be obtained[7].

Microencapsulation of dye intermediates in oil can also be carried out by interfacial polycondensation. by such polycondensation techniques, a thin, high molecular weight polymer film can be produced as capsule shell. The process comprises bringing two reactants together at a reaction interface between the two mntually immiscible phases, whereby, instantaneous formation of a film insoluble in the parent media of the reactants take place. Capsule shell of high molecular weight polymers are insoluble in organic solvents and infusible in hot melt coating temperatures. Varieties of polymers such as polyamides, polyurethanes, polysulphonamides, polyesters, polycarbonates and polysulphonates can be used for encapsultating a variety of materials. The microcapsules can be prepared in slurry form over a wide range of solid contents with only minor adjustment of process conditions. Microcapsule slurries can be spray dried. The dried microcapsules can be redispersed in aqueous media and can be coated over paper with no appreciable loss in quality and print intensity of the copies. Microcapsules manufactured by the interfacial polycondensation technique can be coated on paper at a low coating weight to give optimum print intensity under normal writing or typing pressure. In situ polymerisation of mono- or prepolymer smers at an oil-water interface and spray drying techniques are also being utilised now for micro-encapsulation of dye intermediates.

With these improved process, synthetic microcapsules with higher solid contents 30-50% can be obtained and as the microcapsule with little variation in diameter are made, the coating weight of donor surface can be reduced to about 4 gm/m^2. Moreover coating can be done in high speed coaters.

The colourless dye intermediates used in the carbonless copy paper are selected from available derivatives of triaryl methane, diphenylmethane, xanthene, thiazine, spiropyran and fluoran compounds. The most important colour formers of first generation that are commonly in use are crystal violet lactone, malachite green lactone, benzoyl leucomethylene blue, Rhodamine B -lacton, leucoauramine, O-hydroxyl benzyl acetophenone and many leuco compounds of dyes of the indamine, azine, oxazine, thiazine and carbazole series and also pyridine carboxylic acid lactones are in use. Due to increased use of Electrophotographic copy systems, copies of excellent xeroxability have become necessary with improved contrast and higher number of copies. Improved colour formers like the fluorans are today the most important group of new colour formers which have been introduced into the field of chemical carbonless copy papers within the last years[10,11].

In the carbonless copy paper system, the liquid nuclei of the capsules coated on the donor surface, contains one or more organic dye intermediates, which take part in an electron donor acceptor solid surface chemical reaction, giving distinctive colour with inorganic substance coated on the receptor surface. The solid inorganic material is in fine particle form and is adhered on the surface of the paper with the help of an adhesive material. Numerous developments have taken place and the colour acceptors used today in chemical carbonless system differ totally from inorganic clay like materials used earlier.

Recent development of the carbonless copy paper is that the two coating systems employed may be incorporated in the same surface by modern available techniques. The duplicating papers produced by this technique are termed as "Self copy papers" in which both the capsule and the clay are coated on the same side of the sheet. The problem of premature development of colours in such a manifold system are prevented by applying an intermediate coating or by incorporating clay like material during capsule formation[12,13]. The most recent trend in the 'Self copying paper' is to form sheets from paper stock in the sheet making machine, not by coating the microcapsules on paper. In this system, the capsules of colour producing leuco-dyes and colour activating chemicals are included with the fibre, size and other materials of the paper during its manufacture on the paper machine. The Self Copy paper prepared by this way can be imaged by type-key, pen or pencil. These papers are extremely pressure sensitive and they produce permanent colour formation.

Hundreds of methods for producing microcapsules and thereby making carbonless copy papers are cited in the patent literatures. The earliest patents by B.K. Green[14,15,16,17] of National Cash Register Company, USA are the landmarks in carbonless copy paper system. Later technology may be regarded as developments on the systems introduced by B.K. Green et al.

WORLDWIDE MARKET :

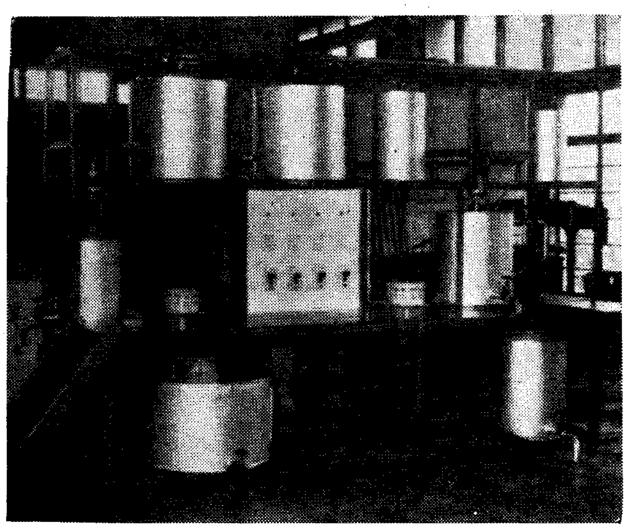
The first carbonless copy paper appeared on the US market in 1954. Soon after Wiggins Teape, the leading fine paper company of U.K., took licence from the National Cash Register Company, USA for exclusive production and sales rights in Europe. In Japan, the system was worked out by three independent paper companies and all of them are already active in production of this paper. Wiggins Teape in U K. has also undertook independent research and developed their commercial product with new concepts.

The main Carbonless Copy Paper producing companies are Wiggins Teape, Reed Paper and Dickinson Robinson Group in U K., Koehler, Zanders, Feldmuhle in West Germany, Appleton Papers, Mead Corporation, Nashua Corporation, Moore Business forms etc. in U.S A., Jujo, Kanzaki, Fuji and Mitsubishi paper mills in Japan, Copigraph, Voiron in France etc. The United States, Europe and Japan are the three main markets of Carbonless papers. The production capacity of USA in 1981 was 4,80,000 tons, while that of Japan and U.K., the production capacities were 2,50,000 tons and 1,15,000 tons per year respectively[18].

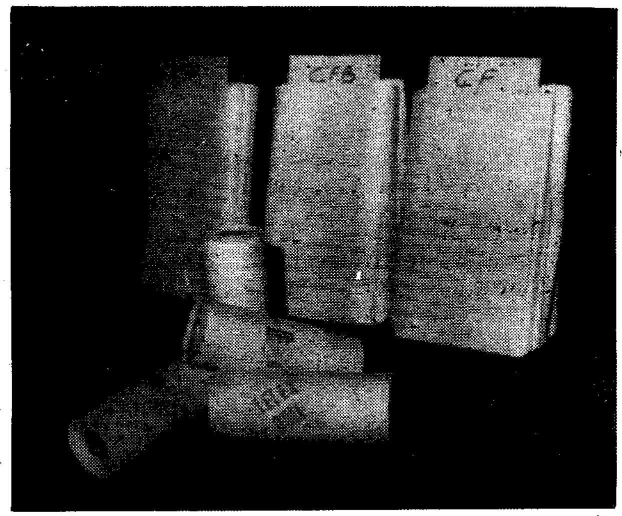
The production capcities of the other leading producers of carbonless copy paper in 1981 were – Belgium (95,000 tons/yr.), Germany (70,000 tons/yr.), Spain and Italy (21,000 tons/yr. each), France (20,000 tons/year) etc [18]. Other countries with small production capacities are Yogoslavia, Finland, Switzerland, Mexico, Brazil, Agrentina, Venezulea, Korea, Australia and South Africa.

INDIGENOUS TECHNOLOGY :

Indigenous technology is now available for manufacture of this paper. The Regional Research Laboratory, Jorhat, has developed process know-how, which involves microencapsulation of colourless dye intermediates and then preparation of donor and receptor coating mixes. The coatings are applied by a coating machine and coated papers are dried at controlled temperatures. Photograph shows a 50 kg/bath pilot plant for microencapsulation at RRL, Jorhat. Commercial production of the paper has recently been started by one of the licencees, based on RRL technology.



Microencapsulation Pilot Plant (50 Kg/Batch) At RRL, Jorhat



Products of Carbonless Copy Paper Produced By RRL Knowhow

CONCLUSION :

Undoubtedly, there has been tremendous development of the chemical carbonless copy paper technology during the last three decades or so. Though the cost of these papers is generally higher in comparison to many other copying papers, their cleanliness, higher efficiency and other innumerable advantages are helping them to gain extensive market. It is expected that the total world consumption will be doubled by 1987 and will most probably be trippled by 1991.

In our country, with the sophistication in the business and industrial fields, there will certainly be a great demand for this paper. It is also expected that there is a vast scope for exporting this paper to the Middle East and other developing countries.

ACKNOWLEDGEMENT :

The authors are highly thankful to Dr. J.N. Baruah, Director, Regional Research Laboratory, Jorhot, for his kind permission to publish this paper.

REFERENCES :

1) "Copying paper market offers considerable growth potential" Paper, Vol. 186, No. 3, P. 135 (Aug. 9, 1976)

2) Asajii Kondo "Microcapsule processing and Technology" P. 11-17, Marcel Dekker, Inc. New York(1979)

3) Howard W. Mattson, "Miniature Capsules" International Scienee and Technology, New York P. 66-76 (April, 1965)

4) Harvard Business School, "Report on "Microcapsulation" Management Reports, Boston, Mass (1965)

5) Hans. F. Hubber and Howard G. Stroble "Capsular Adhesives" TAPPI, Vol. 47, No. 5, P. 41 A-44 A (May, 1966)

6) Russel E. Phares, Jr. and G.J. Sperandio "Coating pharmaceuticals by coacervation" Journal of Pharmaceuticals Sciences, Vol. 53, No. 5, (May 1964)

7) H. Ruus, US Patent 3, 429, 827 (Feb. 25, 1969)

8) Richard Dlae Shackle and Gerhart, Schwab US Patent 4, 010, 292 (March 1, 1977)

9) Fuji Photo Film Co. Ltd, US Patent 1, 436, 798 (May 26, 1976)

10) F X. Brunner, 'Dye-stuffs for chemical carbonless copy papers', Ciba-Geigy Ltd., Basle, Switzerland.

11) Yasuhiro Ogata, Noburo Hibino, US Patent 4, 104, 910 (Aug. 8, 1978)

12) David N. Vincent and Ronald R. Golden, US Patent 3, 906, 123 (Sept., 16, 1975)

13) Fuji Photo Film Co. Ltd., US Patent 1, 436, 798 (May 26, 1976)

14) B K. Green and Lowell Schleicher, US Patent 2, 730, 456 (Jan. 10, 1956)

15) B.K Green and Lowell Schleicher, US Patent 2, 730, 457 (1956)

16) B.K. Green and Lowell Schleicher, (US Patent 2, 800, 457 (July 23, 1957)

17) B.K. Green, US Patent 2, 800, 458, (July 23, 1957)

18) F.X. Brunner, Pulp and Paper International, Vol. 24, No. 5 (May 1982).