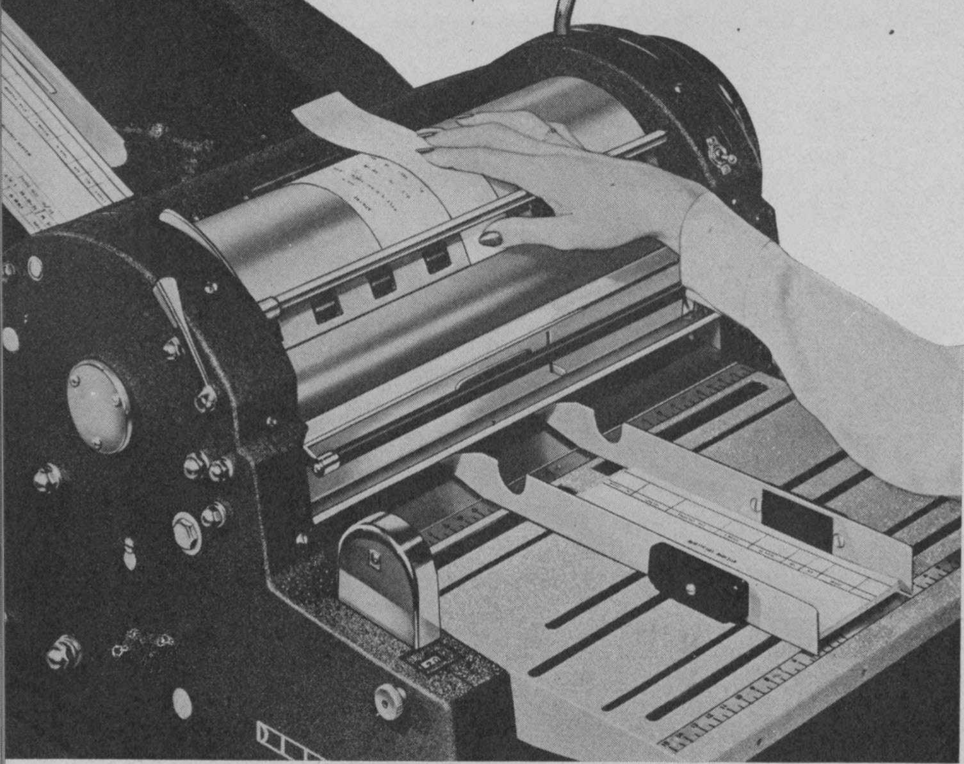

Machine widely used to run copies of parts and assembly orders in aircraft industry. This model has block-out strip which omits undesired data.

Photo: Ditto, Inc.

The Chemistry of Duplication

The author, who has a score of patents in this field issued or pending, correlates in this article processes and products in duplication industry as reflected or disclosed in patent literature.

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THE duplication industry has much in common with photographic manufacturing. In merchandising, both of these industries largely depend on the supplies, and view their machines principally as mechanical salesmen, which will secure a continuing volume of supply sales. Chemically, both deal with a multitude of variables, bordering almost on intangibles, in such diverse fields as surface chemistry, catalysis and colloids. And both of these chemical specialty industries have followed a policy of close secrecy in processes, waived only in the few instances when readily enforceable patent protection could be secured:

This article will discuss and correlate processes and products in the duplication industry, in so far as they are reflected or disclosed in the patent literature.

Though all printing is duplication in a broad sense, we shall here consider duplication in the more generally accepted meaning of the word, to signify the production of a relatively short run of copies on machines that can be handled by an office girl after a few hours instruction.

The commercially successful duplication processes may be divided into the following principal groups:

I. Hectograph Processes:

Write or type with ink containing a soluble dye.

Contact writing with *gelatinous mass* into which the dye diffuses.

Contact the mass with successive copy sheets, into which the dye is adsorbed from the mass.

This process is the most economical where less than 100 copies are required, and is characterized by extreme adaptability to different business systems and machines.

II. Solvent Process

Type or write on paper against special aniline dye carbon paper, so that a dye carrying mirror-reverse dye imprint is formed.

Place this mirror-reverse dye imprint on revolvable metal drum.

Contact mirror-reverse dye imprint with successive copy sheets, which *have been pre-moistened with an alcoholic solvent.* The solvent dissolves a part of the dye, thus causing transfer of some dye from the master imprint to each successive copy sheet.

This process is the most economical where about 100 to 400 copies are required; is characterized by extreme convenience in operation, corrections and alterations.

III. Stencil Processes:

Type or write on *stencil,* so that the stencil is perforated at points of writing.

Place perforated stencil over an ink supply, so that ink penetrates perforations in stencil.

Contact stencil with successive copy sheets, so that ink *penetrates stencil* in written parts, and thus prints on copy sheets.

This process is the most economical where more than 500 copies are needed; is adapted to straight run duplication rather than to business systems.

Chemistry of the Hectograph Process

The hectograph process is doubtless the chemically most complex of the duplication processes, as the hectograph gel is fundamentally a dye *solvent* (not *adsorbent*) gel. About 300 years ago, clay-water-honey compositions were used, to be later superseded by gelatin gels plasticized with glycerin, carbohydrates[11, 13, 70] and more recently also with glycol solvents,[91, 124] sulfonamides, sodium lactate[15] sorbitol[143] glyceryl and glycol phthalates[134] et cetera. The proteins have been predominatingly though not entirely of animalic origin.

The necessary resistance to atmospheric conditions is imparted to the gels by tanning agents,[58, 78] which by more or less gradual action increase the resistance of the gel. The desirability of tanning a gel to the correct hardness,[5, 6] and arresting action at that point is a challenging problem, and one which is common to duplication and photographic industry. Attempts have been made to solve it by pH adjustments,[111] choice of tanning agents, addition of tanning retardants,[147] removal of excess tanning agents,[148] and photochemical tanning.[28] The most effective methods, however, have not yet been published and the pertinent patents may not issue for another year.

This problem of controlling tanning reactions may have considerable potentialities in medicine and gerontology.[141]

The amounts of acetaldehyde normally contained in human blood,[143] would amply suffice to tan completely the body proteins, in a matter of months. Such tanning is a cause of the rigidity, which occurs within a few hours after death.

cal side reactions, or it may be due to the formation of a tanning bridge in some particular position in the protein molecule. In either event, the result is that cumulative tanning of body proteins, which we know as old age.

The copy strength, or intensity of the copies from the hectograph gel, is governed by numerous factors. Significant are solvent power of the plasticizer for the particular dye employed,[15] and the ratio of solid to liquid in the gel composition as well as the gel strength of the protein constituent. Anything that influences diffusion of dye likewise affects copy strength, and the hectograph industry is able to produce gels in which any given dye will diffuse at any desired rate of speed within very wide limits, without changing appreciably any other properties of the gel.

One of the expedients used for this

contact with the copy sheets—excessive tack leads to tearing of paper on the machine, damage to the surface of the hectograph mass, and other related complications. Generally speaking, tack is influenced by the type of protein employed, the acidity, the composition of plasticizer, certain ions, gums,[61] starch or the like,[4, 8] and modes of treating the mass while in a melted state. Tanning agents,[44] or soaps,[63] reduce tack, and thereby increase the number of copies obtainable. The mass may also contain antiseptics,[9] pigments,[34, 35] et cetera.

Several types of surface lubricants have been used to prevent sticking together of hectograph films or blankets in the process of handling in the plant,[17, 20, 27] when newly manufactured.

The surface cohesion of the mass is another very important characteristic. If this cohesion falls below a certain critical

In one operation Ditto's gelatin machine will reproduce eight colors. These colored inks are laid down on a master copy with pen or water color brush.

In the living organism, this tanning is counteracted by (A)—the directional tanning under influence of repeated stretch and (B)—the continued state of flux in the protein molecules, which are continually split and re-synthetized. In this interplay of synthetic and splitting reactions, the protein molecules are broken down before tanning has gone very far, and resynthetized in a non-tanned state.

The aging of living organisms I believe is due to the occasional formation, by tanning, of bridges between protein molecules, which cannot be broken by the cell enzymes. Such irreparable tanning may be caused by tanning agents foreign to the organism, or formed by unusual biologi-

purpose is to emulsify in the hectograph mass, before gellation, a material nonsoluble in the plasticizer. The ultra microscopic globules of this emulsified material will impede diffusion of the dye by surface effects or by simply interposing nondye solvent particles in the path of diffusion of the dye. Many of the various copy brightening agents patented[133, 134, 139, 142] depend on this principle; others on the increase of dye solvency,[15, 137] or on obscure surface effects.[24, 51, 90, 124]

The brightness of copies, and ease of handling also depend on the degree of tackiness of the composition, which must be carefully controlled. A certain amount of tack is necessary to secure adequate

minimum under the influence of heat and humidity, then the adhesion to certain coated types of copy sheets may exceed the cohesion of the mass, so that particles of the mass loosen from the surface, which is thus destroyed. Cohesion is generally impaired by anything that increases the brittleness of the mass—excessive tanning is the most common influence in this class.

Another chemical problem in hectograph duplication is to secure a firm adhesion or "bond" to the cloth[3, 131] or high wet strength paper,[115, 127, 140, 10] which serves as the backing for the hectograph gel. The solutions found here may be of an interest far transcending that of duplication industry, since the task of securing adhesion between a protein and a base material is a rather general one. Means employed for this purpose include applying to the backing materials coatings of oils which on oxidation give off tanning decomposition products,[2] adsorbent montmorillonite type clays, tanning agents,[21, 114] carried by nitrocellulose type lacquers,[25] mutual solvents or plasticizers[31, 32, 36, 130] and various non-tanning ingredients.[37, 144] For an understanding of the bonding phenomenon it is important to keep in view that a bonding agent is a substance which has affinity both for the protein mass and for the adjacent backing. This usually is a lacquer coated cloth or paper of high wet strength, although other materials have been contemplated.[1, 12, 16, 22, 145]

Obviously all tanning agents which can be imbedded or adhered to a lacquer coating, will bind the protein material.[25] However, a great number of substances which are not tanning agents have the same properties. To have tanning properties, a substance must comprise at least *two* groups capable of reacting with different protein molecules so as to tie these together. For bonding purposes, it is sufficient that the substance have *one* group capable of becoming attached to the protein molecules, provided the rest of the molecule is adapted to becoming anchored to an adjacent coating of a different material. As is the case in all surface phenomena, the bonding is greatly affected by conditions of application and by any preceding treatment of the protein gels or of the bonding agent itself, as well as of a great multiplicity of other physical variables. While protein masses have been the most successful practically, numerous attempts have been made to utilize other types of gelling ingredients, such as agar-agar,[7] synthetic resins,[19] and cellulose derivatives.[42]

When copies have been taken from the hectograph mass, it is important that the dye disappear over a reasonable period of time so that the surface can be reused. This disappearance of dye is referred to as "clearing." Clearing occurs—A. By absorption of the dye to that part of the backing which will contact it when the hectograph blanket is rolled up and B. By diffusion of the dye into the interior of the mass and retention of the dye at that side of the backing which is covered by the mass.[64] Special ingredients may be used,[121] and the rate of clearing is profoundly affected by the composition and formulation of the hectograph mass. Any change in composition which reduces the speed of diffusion will increase copy strength, but reduce speed of clearing.

Photo: Ditto, Inc.

Air lines keep pilots supplied with weather reports and huge weather maps copied on flat bed duplicators such as this. Apparatus is easy to use.

The Solvent Process

In solvent process duplication, the chemical aspects are considerably less involved, although by no means so simple as they may appear. The solvent liquids contain a highly volatile ingredient in major proportions, and a substantially very much less volatile ingredient adapted to soften the master impression so as to increase the amount of dye transferred on each contact, and possibly also agents to prevent corrosion of metal parts contacted by the liquid, denaturants, agents to reduce flammability, and the like. The conventional duplication solvents are based on methanol which has the advantage of high volatility and a rather mild odor, but the great disadvantage of toxicity. More recently developed liquids,[14, 30, 146] are based on the non-toxic ethanol in combination with small amounts of other solvents which, by forming balanced constant boiling mixtures, impart to the composition sufficient volatility. Fluorinated hydrocarbons of the "Freon" type have been used to reduce flammability.[135]

In some cases, the liquid in the solvent process may be applied to the back side of the master.[45, 49, 54, 65]

In the dye carrying carbon papers used for making master impressions for the solvent process, it is naturally not necessary that the dyes employed be water soluble. On the contrary, water non-soluble dyes,[26, 46] generally have a superior fade resistance. Dyes soluble only in acid media have been used in conjunction with acidic liquids.[50] However, it is often desirable to use the same dye for hectograph and for solvent duplications, as these processes may be used to supplement each other in composite installations.

The dye carrying and depositing supplies such as carbons and hectograph ribbons are of crucial importance to the hectograph as well as to the solvent process. The number of copies and their brightness is limited by the amount of dye deposited and can be increased beyond a certain limit only by improvement in the carbons and ribbons. The intensity is governed by the character of the dye selected,[112, 128] the hardness and composition[94, 116, 117, 120] of the wax material vehicle,[132] mode of incorporation of the dye in the vehicle and the extent of subdivision or comminution of the dye, as well as on the presence or absence of unconventional ingredients[33, 62, 118] and pre-treatments of the base cloth material.[119] All of these factors have to be adapted to the particular application in view.

In recent years, the use of printed solvent process duplication masters has been vastly extended. For many applications printing inks are formulated in which the hectograph dye takes the place of the conventional pigment and the vehicle is either a solvent for this dye,[125] or sufficiently soluble in the other media with which it is contacted to release the dye particles in a state free from any non-solvent film. Certain specialty printing processes have been employed.[48, 136]

Much progress has been made in recent years in the problem of fade resistance. The dyes which have the highest tinctorial strength are unfortunately rather susceptible to fading when exposed to direct sun light. However, they can be protected from this action by incorporating light filtering substances in the duplication supplies, by including dye mordanting agents in the copy paper,[23, 43, 52, 56] or in the solvent. In this manner, the dye is transformed in the paper to an insoluble form which is substantially non-fading and which can be guaranteed to last more than one hundred years under ordinary office conditions. These improvements have greatly contributed to the wide spread and increasing adoption of the hectograph duplication process by insurance companies where permanency of records for the maximum human life time is prerequisite.

The character of the copies is largely influenced by the paper surface. Different types of finishes are required for use with solvent duplication and with hectograph. In the former case, special ingredients may be employed to precipitate the dye and prevent blurring or penetration in the paper. In the case of hectograph duplication, a highly porous paper will produce bright copies and a limited run, while lower porosity of the paper results in a longer run of less brilliant copies. Surface treatments of the papers with wetting agents,[120] and special solvents[18, 29, 53] have been recommended in certain instances.

The papers used for making the master impressions present a problem no less complex. In the case of the hectograph process, it is important that these papers present surfaces impermeable to oily ribbon inks.[59] With solvent process duplication,[44] it is necessary to control closely the adhesion properties between the paper and the wax vehicle that carries the dye in the paper surface, as otherwise the dye impressions from the carbon paper would be insufficient in volume or too broad. In master paper, the hygroscopicity characteristics are highly significant as this type of paper is widely used for printing with hectograph printing inks, and therefore must not curl or present other difficulties in handling on printing presses at high speed.

The Stencil Process

The stencil process is chemically far less complex. The stencil inks are mainly solutions of dark dyes in glycerin type solvents,[66] or in oil type media.[88] Since the tinctorial strength of the dye in each impression needs to suffice only for one copy, no need exists for the use of high intensity dyes and the formulation is correspondingly simplified. The principal requirements are that the ink penetrate the stencil without build up and that it does not spread or "feather" excessively. Naturally, the vehicle of the ink must not affect the coating of the stencil. This coating is either a cellulose ester;[67, 68, 97, 98, 99, 100, 107] ether;[101] or a paraffin type coating,[71, 72, 73, 77] although other materials such as proteins,[80, 81, 82, 83, 84, 85, 86, 123] shellac.[87, 89, 95, 96] certain resins,[75, 108, 109, 110, 113] waxes,[74, 76] bentonitic clays,[93] metallic films,[102] nylon type products,[126] agar-agar,[104] nitro starch,[122] or generally organic polymers of elastic character and amorphous structure,[105] may be employed.

Photo: Ditto, Inc.

Many insurance companies make copies of permanent records on gelatin machines. Photo above shows a battery of gelatin machines in office use.

The stencil coating may occlude a lubricating oil,[103, 107] in a finely divided state.

The stencil processes and the hectograph processes can be advantageously combined by employing a special hectograph stencil ink on a stencil machine. Each copy produced in such a manner is a hectograph master, and can be used in turn to make a large number of hectograph copies.

A development of the stencil process is utilized with the Elliott Addressing machines, in which an oleaginous type ink is being impressed through a small stencil, of type adaptable to handling or indexing in business machines. The possibilities of combining this specialized type of stencil duplication with the hectograph process, are very intriguing.

Numerous specialty processes have been developed, but these have not gained commercial importance comparable to the three principal processes just outlined. Various ways of using sympathetic ink reactions for duplication purposes have been patented,[38, 57, 69] and are being resubmitted to manufacturers every year by hopeful inventors.

Methods of copying matter written or printed with ordinary record inks, have been considered since very early dates.[39, 40, 41] It appears that photographic methods combined with stencil[79, 92] or hectograph[47, 138] duplication will provide the most economical solutions of this problem.

The concept of duplication is as old as the commercial use of writing. The seals or signets used commonly in the Near East several thousand years before Christ, are nothing but duplication instruments, obviating the need for re-writing in the laborious style of those days. An inscription in negative obviously made by impression, has been found in Persia, which dates from the third century A. C.

The growing complexity of transactions and the concurrent development of mechanical bookkeeping and writing means, have necessitated a corresponding development of duplication.

Today, no need exists for re-typing in connection with the numerous reports and data required by the complexities of accounting, sales analysis and control, or reports to government agencies. All the information required for these various purposes is typed but once, and the requisite number of reports are made in a matter of seconds by running through machine blanks prepared to record or to omit any selected portions of the data, as needed by the various departments. The executive file report showing all the data relating to the transaction is made from the same typing as the label, which shows only the address of the customer. The time thus saved, and the elimination of errors on re-typing, is today saving literally millions of hours and dollars for defense and other industries.

Looking toward the future, one might

foresee still closer connection between duplication and all other types of business machinery, a greater differentiation between supplies adapted for specific requirements in copy strength and intensity, and the advent of new processes to keep pace with the ever changing complexities of our needs.

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