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DESICCATING BARRIERS
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ABSTRACT

This report covers work performed under the second period of the contract.

The aim of this study is to develop new and superior packaging systems and materials capable of producing a dehumidified or moisture controlled atmosphere similar to that presently produced by Method II of Specification MIL-P-116D, at a lower cost and greater efficiency.

The work during this period has consisted mainly of work on desiccating materials capable of producing the desired effect when used in conjunction with barrier material components.

The work is continuing in line with presently promising results.
Introduction - The major part of the work during this period has centered around the desiccating portion of the barrier. If we consider the barrier as a sandwich consisting of an outer, highly moisture resistant layer; a middle, desiccating layer; and an inner, grease-proof, heat sealable layer, it is evident that this middle layer deserves the major part of the research, since the qualities desired in the other layers have been researched quite extensively in the past.

It may be well to re-state the basic design targets:
1. Water vapor resistant after flexing at 130 and -20 F.
2. Optically clear to permit identification of parts in an envelope.
3. Stable, durable, non-blocking and heat sealable.
4. Resistant to oils, greases and hydraulic fluids.
5. Offering a high degree of corrosion protection.
6. Relatively low in cost by comparison with Method II.

Progress Report - The film-forming materials most extensively investigated during this period: animal glues, gelatin, polyvinyl alcohol and vinyl solutions. The desiccating additives to these films were calcium chloride, lithium chloride, glycerin and combinations thereof.

All of these materials show considerable promise, but none of those tested to date show all the characteristics desired. In brief, we are on the right road, but the goal is not yet in sight.

A brief summary of some results is given on the following page.
Film - Desiccant Combinations, with Comments.

Gelatin - Forms a glass clear film, even with high proportion of desiccating salts (4 to 1 ratio of salt to gelatin). Highly adhesive until bone-dry. Extremely brittle at low temperatures even when plasticized with glycerin, soluble oils etc. when dry, flexibility increases with added water content. Plasticizers tend to sweat to the surface. Tendency to burn on heat sealing. Tendency to form mold and mildew when moisture content increases, even with complete sandwich, such as polyethylene - gelatin - polyethylene, mold colonies form spores deposited during lamination. Would be relatively low in cost, if other qualities could be attained.

Poly-vinyl alcohol - Forms a clear, heat sealable film, and the process of heat sealing tends to increase its imperviousness to water. Will tolerate desiccating salts in all usable proportions. Easily plasticized with glycerin for low temperature flexibility though -20 F for the un laminated film has not yet quite been attained. Like gelatin, has considerable built-in hygroscopicity. Rather poor adhesion when dry to the more common plastic components such as polyethylene. Relatively impervious to gases, good oil and solvent resistance, tensile strength and tear resistance. Relatively high cost, but this may be offset by other advantages.

Lithium Chloride - A very active desiccant -- perhaps to activate for production use. Relatively expensive.
Calcium Chloride - Probably the most likely desiccant, alone or in combination with small quantities of lithium chloride. Very inexpensive in terms of moisture absorption.
Additional investigations - One other area of investigation is worth mention. Calcium chloride was used as a pigment in solutions of vinyl co-polymers in acetone and methyl ethyl ketone. The cast film so obtained was then top-coated with additional vinyl to cover the 'pigment' of calcium chloride. Such a film has relatively high water absorption characteristics, but is virtually opaque (white) due to the calcium chloride. On the other hand, when a water solution of poly-vinyl alcohol and chloride is used, the resulting film remains virtually transparent.

Prospects for the future - Perhaps the easiest and most constructive way to summarize results so far is to indicate the general direction of future work.

Poly vinyl alcohols, in conjunction with other films, seem to be the best prospects for the intermediate desiccating layer of the film. A typical construction for a complete barrier might be something like the below diagrams:

- **Mylar**, for the outside layer, to impart strength, relatively high resistance to heat as in the heat sealing operation, relatively dimensionally stable and virtually optically clear at \( \frac{1}{2} \) mil thickness.
  Cost - about \( \$0.9 \)/ sq. ft.

- **Polyethylene**, high density and molecular wt. for low moisture vapor transmission, fairly high melt index. Fairly transparent at 6 mil thickness.
  Cost - about \( \$1.4 \)/ sq. ft.

- **Poly-vinyl alcohol**, plasticized with glycerin ethylene glycol, etc. and containing desiccating salts, probably a small amount of LiCl and a much higher percentage of CaCl. About 3 mils.
  Cost - about \( \$1.9 \)/sq. ft.

- **Polyethylene**, low density and melt index, for heat sealing. Less than 1 mil.
  Cost - about \( \$0.5 \)/sq. ft.
If these relatively incompatible materials can be put together into one barrier at reasonable cost, the target cost of 5¢/sq. foot would be met, which would be considerably less than the 7¢ to 9¢/sq. foot cost of present barriers for Method II, when the cost of desiccant is included as a part of barrier cost.

There are, of course, many other possibilities. Saran coated polyethylene might replace the Mylar, at lower cost. The interior polyethylene film might be eliminated and an 'un-coated' PVA film used instead, since such a film would heat seal at 300 to 350 °F. PVA, when so heat sealed, tends to extrude from the seam both inward and outward, forming a very thin seam in cross-section which is rendered relatively impervious to water at room temperature by virtue of the heat treatment effected in the act of sealing.

One additional bonus appears to be quite feasible with PVA. A droplet of cobalt chloride indicator solution placed on the film and dried provides a built-in humidity indicator for the interior of the package.

The possibility of using an intermediate layer of some porous material, such as glassine paper, may deserve consideration in future work. If this should be the case, it may be possible to imprint the paper before sizing with a solution of PVA and cobalt chloride. This would produce a humidity indicator within the barrier.

By combining the two indicator methods above, we might achieve an indicator system which would indicate both the "freshness" of the packaging material and the condition of the interior of the package.

The work is continuing, with the emphasis being placed on the materials and processes mentioned above.

For demonstration purposes, this paragraph was photographed for printing through a film consisting of 4 mils of polyethylene, 2 mils PVA.