## Hydroxypropyl Galactomannan- A New Entrant in Paint Industry

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### 1. Introduction

Seed gums (galactomannans) undoubtedly provide a rich and renewable reservoir of structurally and functionally different biopolymers. However, the possibility of functional groups in seed galactomannans to undergo a wide range of chemical reactions is an additional advantage for the extension of their applications. The availability of a spectrum of seed gums thus provides an excellent opportunity for the development of fine tuned products by chemical modification for broader applications.

The growing industrial utility of these gums or their modified derivatives in the field of paper, textile, petroleum recovery, pharmaceutical etc. has resulted in an impetus in India for intensified research on new applications of gums and their chemically modified products. Chemical modifications are intended to enhance the solubility of the galactomannans and to impart some very peculiar behaviors in aqueous solution according to the needs of the particular final application.

Galactomannan is derived from the seeds of plant *Cyamopsis tetragonolobus,* a pod bearing legume (Fig. 1) grown commercially in India, Pakistan and the southwestern United States. The seed is composed of hull (15%), germ (45%), and endosperm (40%). The endosperm contains 75-85% of the hydrocolloid, has a chain of (1$\rightarrow$4)-linked-$\beta$-D-mannopyranosyl units with single $\alpha$-D-galactopyranosyl units connected by (1$\rightarrow$6) linkages to, on the average, every second main chain unit. The ratio of D-mannopyranosyl to D-galactopyranosyl units is about 1.8:1. The average molecular weight of the Galactomannan is in the range of 1-2 $\times 10^6$ dalton.

Galactomannan forms viscous, colloidal dispersion when hydrated in water. It is being used as a viscosity builder and water binder in many industries such as textile, food, paper, petroleum, mining, explosives, pharmaceuticals etc.

As a part of our major research and development activities we have paid a great deal of attention to chemical modification and characterization of Galactomannan with a view to promote industrial utilization of Galactomannan based products. Significant changes in properties occur when the Galactomannan is substituted with the new functional groups.

With a view that hydroxypropyl Galactomannan (HPG) may replace hydroxyethyl cellulose (HEC), which is costlier ingredient being used as rheology modifier in paints, chemical modification of Galactomannan via hydroxypropylation was carried out at lab/commercial level by using our state of the art technology to achieve the desired substitution.

In the present study, HPG (Rheoluc PT$^{TM}$) were employed to prepare water based paints. The water based paints were also prepared from conventional rheology modifiers based on cellulose derivative (HEC). The comparative study of these reveals very interesting findings in HPG (Rheoluc PT$^{TM}$) based paints compositions.


**Fig. 1 (A) *Cyamopsis tetragonolobus*,**


**(B) Seeds,**
**(C) Endosperms**

**2. Paint Technology**

Paint industry is one of the oldest and largest industries in the world. Cave paintings drawn with red and yellow ochre, hematite, manganese oxide and charcoal may have been made by early homo sapiens as long as 40,000 years ago. Ancient painted walls, to be seen at Dendera, Egypt, although exposed for many ages to the open air, still possess a perfect brilliancy of color, as vivid as when painted, perhaps 2000 years ago. The Egyptians mixed their colors with some gummy substance, and applied them detached from each other without any blending or mixture.

Paint is the general term for a family of products used to protect and add color to an object or surface by covering it with a pigmented coating. Paint can be applied to almost every kind of object. It is used, among many other purposes, in the production of art, in industrial coating, as a driving aid (lane markings), or as a preservative (to prevent corrosion or water damage). Paint is a semifinished product, as the final product is the painted article itself.

There are two major categories of paints- architectural or decorative paints and industrial paints. In general terms, all paints have four basic components which impact their properties. These components are:

(i) ***Pigment***- provides color and hiding; some are used to impart bulk at relatively low cost. Titanium dioxide ($TiO_2$) is the predominant white pigment. Color pigments provide color by selective absorption of light. There are two main types of pigments:

- Organic: these include the brighter colors, some of which are not highly durable in exterior use. Examples of organic pigments are phthalo blue and hansa yellow.
- Inorganic: generally not as bright as organic colors (many are described as earth colors), these are the most durable exterior pigments. Examples of inorganic pigments are red iron oxide, brown oxide, ochers and umbers.

(ii) ***Binder***- binds the pigment together, and provides film integrity and adhesion. The binder is a very important ingredient that affects almost all properties of the coating, especially:

- adhesion and related properties like resistance to blistering, cracking and peeling.
- other key resistance properties like resistance to scrubbing, chalking and fading.
- application properties like flow, leveling and film build, and gloss development.

With no pigment present, most binders would dry to form a clear, glossy film; some binders are used without pigments to make clear finishes and varnishes.

(iii) ***Liquid/ Carrier***- provides desired consistency and make it possible to apply the pigment and binder to the surface being painted. For most oil-based paints, the liquid component is paint thinner, which is a combustible solvent made primarily of mineral spirits, a petroleum distillate of aliphatic hydrocarbons. For latex paints, the liquid is primarily water.

With the introduction of the European Union (EU) directive in 2004 limiting the emissions of volatile organic compounds (VOCs) in paints and coatings, paint technologies have been shifting from conventional solvent-borne systems towards lower or zero VOC technologies to comply with environmental legislation. These technologies include water-borne, high solids and solvent-free systems. This move spells good news for suppliers of rheology modifiers, which form a critical part of such emerging technologies.

Water borne systems are one of the alternatives as VOC emissions are significantly reduced by applying the same. Besides this, water borne paints offer excellent surface properties including gloss, rub resistance, anti-sealing effect and non-yellowing of film and are easier to apply and clean up.

(iv) ***Additives***- low-level ingredients that provide specific paint properties such as mildew resistance, defoaming, thickening, good flow and leveling. There are many additives which are used in the paint such as rheology modifier, surfactants, defoamers, biocides, drying agents etc. **Here, only rheology modifiers will be discussed as we have aimed to produce the same by hydroxypropylation of Galactomannan .**

Rheology modifiers play an important role in influencing certain key properties of paint technology- for instance, vertical flow, leveling, sagging and sedimentation tendency. The key challenge for suppliers, therefore, is likely to be in developing high-performing products that meet the differing requirements of the new paint technologies.

Rheology modifier provides:

- adequate viscosity (thickness), so the paint may be applied properly.
- impact how thick the paint goes on and how well it flows out when applied.
- modern rheology modifiers help latex paints to:
  - resist spattering when applied by roller.
  - flow out smoothly.
  - be less likely to spoil than with older generation thickeners (with spoilage, the paint may smell putrid and/or lose viscosity).

The choice of the most suitable rheology modifier is a key step in coating formulations. Whether the formulator wants to thicken its coatings by increasing the medium viscosity or to impart pseudoplasticity or thixotropic flow behavior to paint, they will use one of the main rheological additives from the list below:

- Non-associative synthetics- acrylates etc.
- Cellulosics- CMC, HEC, MC, HEC, MHEC etc.
- Organoclays- bentonite and hectorite.
- Organowaxes- castor oil derivative and polyamide-based oragnowax.
- Metal organic gellant- titanates and zirconates.
- Natural gum derivatives- guar or starch derivatives.

We have developed rheology control agent and modifier (Rheoluc PT$^{TM}$) by hydroxypropylation of Galactomannan to control the flow properties of water based coatings such as acrylic water based distempers, emulsion paints (both interior and exterior grades), water based cement primers and water based resin emulsions.

**3. Production of HPG (Rheoluc PT™)**

We have developed a state of the art technology to produce (Rheoluc PT™) with desired level of substitution with certain viscosity of the final product. In this method (Rheoluc PT™) is prepared by the etherification reaction of nonionic propylene oxide reagent with Galactomannan under alkaline conditions (Fig. 2). Such modification greatly improve some specific properties of native Galactomannan like electrolyte compatibility, stability, solubility, and the rheological characteristics in context to their utilization in various types of water borne coatings.

**4. Properties of (Rheoluc PT™)**

Rheoluc PT™ is hydroxypropyl ether of Galactomannan which is non-ionic in nature.

Table 1 shows the important properties of Rheoluc PT™.

Table 1- Properties of Rheoluc PT™

| | |
|---|---|
| Nature | Chemically modified, hydroxypropyl ether of Galactomannan |
| Form | Creamish to beige colored fine powder |
| CAS no. | 68442-94-4 |
| EINECS no. | 270-497-9 |
| pH | 6.0-7.0 |
| Rheology in water | Non-*Newtonian* pseudoplastic |
| Solubility | Excellent in cold and hot water; soluble in water:alcohol upto 70:30 |
| Dispersibility in water | Dispersible with manual stirring. Delayed/controlled viscosity development to allow ease of dispersion and prevention of lump formation. |
| Moisture | Maximum 13.0% |
| Ash | Maximum 6.0% |
| Particle size | Over 60 US mesh (250 µ)- Nil<br>Over 200 US mesh (75 µ)- Maximum 35% |

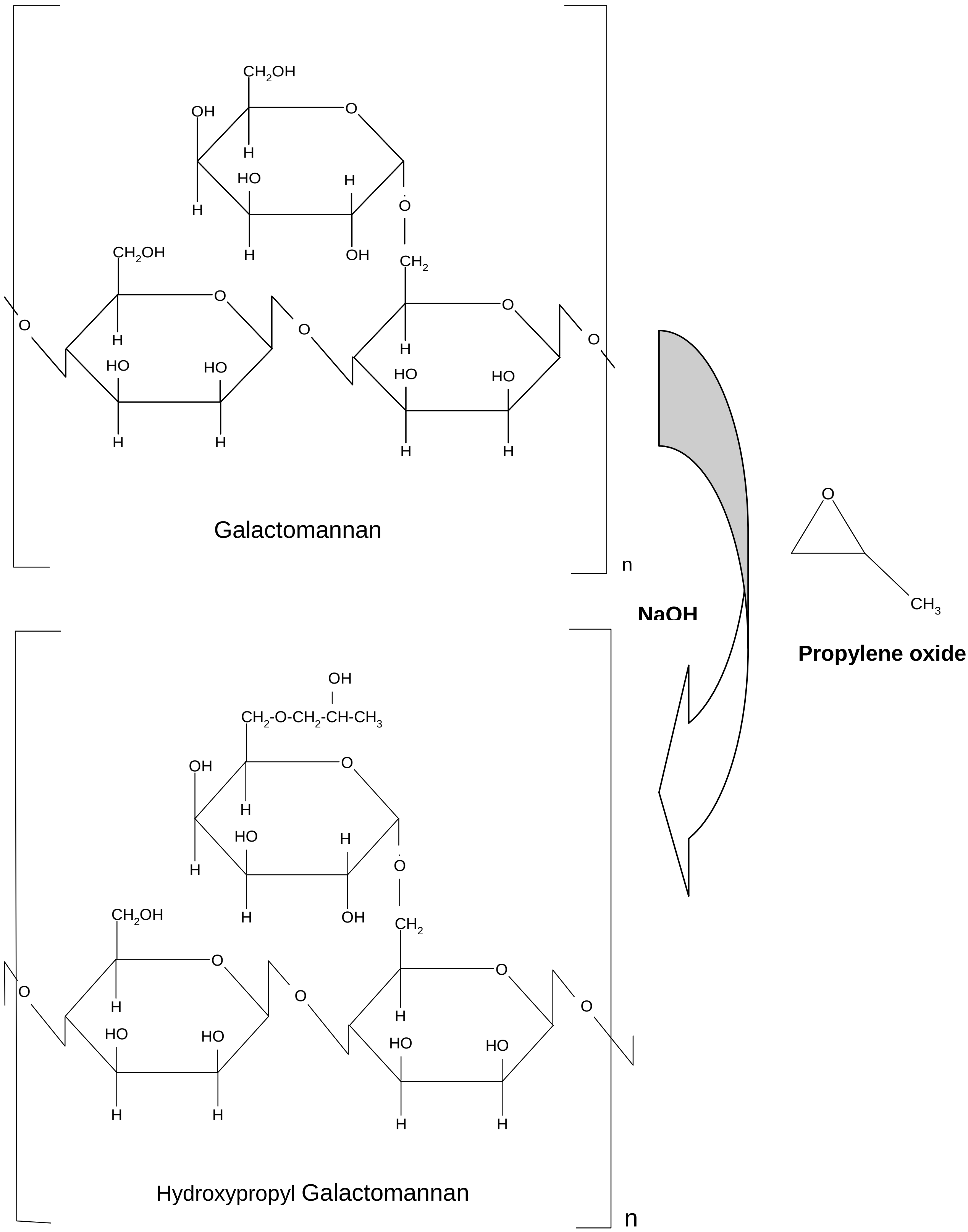


**Fig. 2- Reaction of propylene oxide with Galactomannan**

Rheoluc PT™ is available in three types with differing viscosities:

| ***Viscosity, in aqueous solution, at 25°C, Brookfield (RVF, 20 rpm), cps, solution pH 7.0-8.0*** | | |
|---|---|---|
| | Solution concentration 1% | Solution concentration 2% |
| Rheoluc PT™ LV | 400-600 | 4000-6000 |
| Rheoluc PT™ MV | 800-1200 | 8000-10000 |
| Rheoluc PT™ HV | 1400-1800 | 13000-15000 |
| Rheoluc PT™ Super | 4000-4500 | 25000-30000 |

**5. Comparison of performance of Rheoluc PT™ vis-à-vis HEC**

Following paint recipe (Table 2) was adopted to compare the performance of Rheoluc PT™ and HEC as rheology modifier in paints.

Table 2- Standard paint recipe

| ***Component*** | ***Parts per hundred (by weight)*** |
|---|---|
| Titanium oxide | 5.0 |
| Talc | 31.0 |
| Sodium hexametaphosphate (10% solution) | 1.5 |
| Water | 11.8 |
| Biocide (*P*-chloro phenol) | 0.3 |
| Emulsion (54% solids) | 34.4 |
| Rhelouc PT™ (2% solution) ( 0.32%) | 16.0 |
| ***Total*** | ***100*** |

*Note- The paint recipe followed was a standard formulation in order to comparatively test the performance of Rhelouc PT™ and is mentioned here only as a guideline.*

**5.1 Results**

Performance of Rhelouc PT$^{TM}$ v/s conventional rheology modifier (HEC) is shown in Table 3 & 4.

Table 3- Wet paint testing ( In can properties)

| ***Parameter*** | ***HEC*** | ***Rhelouc PT$^{TM}$*** |
|---|---|---|
| Non volatile matter (%) | 50.2 | 50.5 |
| Weight / Litre (Kg / L) | 1.13 | 1.13 |
| Hiding power ($m^2$ / L) | 4.7 | 5.2 |
| Settling (after 7 days) | Nil | Nil |
| Fungal growth (after 7 days) | Nil | Nil |

Table 4- Dry film testing

| ***Parameter*** | ***HEC*** | ***Rhelouc PT$^{TM}$*** |
|---|---|---|
| Visual observation | Comparable | Comparable |
| Chalking | Nil | Nil |
| Wet abrasion (100 cycles) | Comparable | Comparable |
| UV resistance (100 hours) | No change | No change |

## 6. Conclusion

After conducting various trials, it was found that the Rheoluc PT$^{TM}$ serves as an ideal substitute for products like HEC and other rheological additives on account of its following outstanding properties:

- Requires less energy for dispersion and imparted similar if not better rheological properties with a distinct economic advantage.
- Ease of incorporation into paint formulations.
- Excellent color development and color acceptance.
- Compatibility with a broad range of paint ingredients.
- Compatible with different electrolytes present in paint formulations.
- Batch-to-batch uniformity.
- Forms highly viscous, homogenous colloidal dispersions when added to cold water.
- Very low water insolubles.
- Solution's viscosity increases exponentially with increasing concentration.
- Excellent resistance to shear degradation.
- Solution is stable at wide range of alkaline pH.
- Shelf life of the solution is 6-7 days at ambient temperature.
- Solution is thermal stable between 40$^{o}$C to 70$^{o}$C.

As per the above mentioned findings, it is concluded that in present scenario where the cost cutting plays a vital role in market competitiveness, Rheoluc PT$^{TM}$ provides a better platform to think of.

Rheoluc PT$^{TM}$ is a perfect choice of rheological agent which governs excellent properties for aqueous paints. This product have similar / better properties of HEC and readily available at competitive prices.

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