

# Modeling oil paint network formation

Jorien Duivenvoorden<sup>1</sup>,

Supervisors: dr. I. Kryven<sup>1</sup> & prof. dr. P.D Iedema<sup>1</sup>

<sup>1</sup>Van 't Hoff Institute for Molecular Science, University of Amsterdam, Amsterdam, Netherlands

Email: jorien.duivenvoorden@student.uva.nl

## ABSTRACT

Polymerized oil paint is a strongly cross-linked network and analysis of the molecular topology is practically impossible. Insight in the structure is crucial to explain several degradation processes. In this study an advanced model, based on kinetic Monte Carlo and graph theory, is developed that simulates the formation of an oil paint network and provides the desired structural information. The basic assumption is that the reactivity of the monomers depends on their ability to form cross-links. The addition of three novel routines makes the model approach a real chemical system more accurately. Furthermore, an experimental validation of the model is discussed.

## Keywords

Oil Paint, Polymers, Simulations, Graph Theory, Kinetic Monte Carlo

## INTRODUCTION

Since oil paint has first been discovered by Van Eyck in the early fifteenth century, it has been a widely used paint medium for years to come. Whether Van Eyck really was the first to use oil paint is disputable, but art historians do agree on the boost that the use of oil paint experienced from this moment onwards. Historically, oil paintings are painted with drying oils such as linseed, walnut, and poppy seed oils.<sup>1</sup> In the drying process of these oils no solvent evaporates, but the chemical structure of the oil changes.<sup>2</sup> Would Van Eyck have known that oil paint is actually a dense, entangled network made from cross-linked building blocks? Nowadays, oil paint has become a popular topic of research and we do know that it is a polymer network.

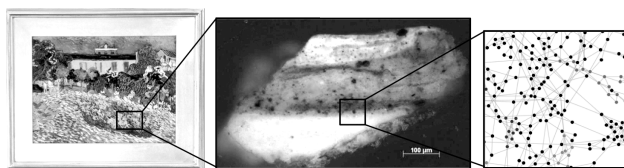


Figure 1 – A cross section of Daubigny's Garden by Van Gogh<sup>3</sup> and a schematic representation of the oil paint network on a molecular level.

This polymer network is a dynamical system that is likely to degrade even when the conditions are optimal. Several degradation reactions have been investigated and the gained knowledge is used to improve existing

conservation methods.<sup>4</sup> Another process that leads to the degradation of paintings is the migration of different compounds. Insight in the topology, the molecular architecture of a network, would explain migration. Unfortunately, this structural information still remains a mystery, because of its complex and dense nature. Experimental characterization of polymer networks is rather limited<sup>5</sup>, so basically the only option is to simulate. Because simulations in art research are uncommon, other fields have to be addressed for the simulation methodology. In polymer reaction engineering the deterministic methods, the kinetic Monte Carlo methods, and molecular dynamics are most used. The deterministic methods make use of population balance equations and in order to solve them the system of interest has to be drastically simplified.<sup>6,7,8</sup> Molecular dynamics, on the other hand, describes a system accurately up to the atomic level, but it has high computational requirements.<sup>9</sup> The kinetic Monte Carlo method lies qua speed and accuracy somewhere in the middle.<sup>10</sup> In this study a kind of kinetic Monte Carlo will be employed together with graph theory, a mathematical approach to describe the connectivity of a network. This research, which is an intersection of chemistry, mathematics and art conservation, will address the challenge of how to preserve these works of art for future generations. The goal is to be able to explain observable processes in oil paintings by elucidating the molecular topology of the network. We propose an innovative model that not only applies theories of polymer reaction engineering to art conservation science, but also introduces novel concepts allowing to capture the polymerization of an oil paint network - a chemical system of great complexity.

## DESCRIPTION OF THE MODEL

The monomers of oil paint are triacylglycerides, or TAG-units, built up from a glycerol molecule bonded via ester bonds to three fatty acids. These fatty acids contain double bonds that are responsible for the formation of the cross-links by reacting with oxygen during the drying process. In order to simulate the polymer network, the monomers have to be simplified and only their most important property, the number of double bonds, is retained. A TAG-unit can be represented as a *node* with a *functionality* that corresponds to the number of double bonds. In other words, the functionality of a node corresponds to the maximum number of cross-links this TAG-unit can make. A node is a graph theory concept and it is basically a dot that can connect to other dots through an *edge*, which corresponds to a cross-link. Slightly different from the functionality is the *degree* of a node, which corresponds to the current number of cross-links a TAG-unit has formed. The information about the

connectivity of the nodes is stored in an adjacency matrix. This is an  $N$  by  $N$  matrix, in which  $N$  is number of nodes, and a 1 in the matrix indicates a connection between two nodes. It is important to realize that the adjacency matrix and the topology contain exactly the same information. Therefore, by analyzing the adjacency matrix, structural information about the topology can be obtained. The reactivity of the monomers determines the topology and this reactivity will be adjusted in the following subsections.

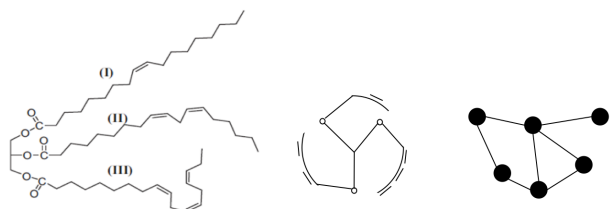


Figure 2 – From left to right: a triacylglyceride, a different representation of this TAG-unit and a network consisting of six nodes.

### Standard model

In the standard model the main assumption from polymer reaction engineering is applied for the first time on oil paint, whose monomers can have functionality up to nine, whereas most industrial monomers have functionality of maximum three.<sup>6</sup> We assume that the reactivity of the monomers depends only on their functionality. Therefore, the probability  $P$  of two nodes connecting is calculated by multiplying the functionality of one node with the functionality of the other, followed by normalization:

$$r_{i,j} = \begin{cases} d_i^{free} \cdot d_j^{free}, & i \neq j \\ 0, & i = j \end{cases}$$

$$P_{i,j} = \frac{r_{i,j}}{\sum_{i,j=1}^N r_{i,j}}$$

Two nodes are sampled from  $P$ , where couples with a high probability of connecting have a higher chance of being sampled, and a 1 is placed in adjacency matrix  $A$  at the corresponding position:

$$A = \begin{cases} 1 & \text{if nodes } i \text{ and } j \text{ are connected} \\ 0 & \text{if nodes } i \text{ and } j \text{ are not connected} \end{cases}$$

After this, the degrees of these nodes are updated and a new pair is chosen, until all possible edges are formed and at this point, the network has reached full conversion.

### Results of the standard model

Figure 3 shows one of the results obtained from the standard model. In order to interpret this plot, a few concepts have to be explained. When monomers start to connect they form small molecules. This stage of the network is called *sol* and the system is in a liquid phase. At some point, the *gel point*, the biggest molecule reaches a critical size and starts to consume all other molecules. The system now becomes solid and this is called the *gel*. Experimentally, the gel point is visible as a jump in viscosity. In the end, all the monomers are involved in this giant molecule and the gel fraction is 1.

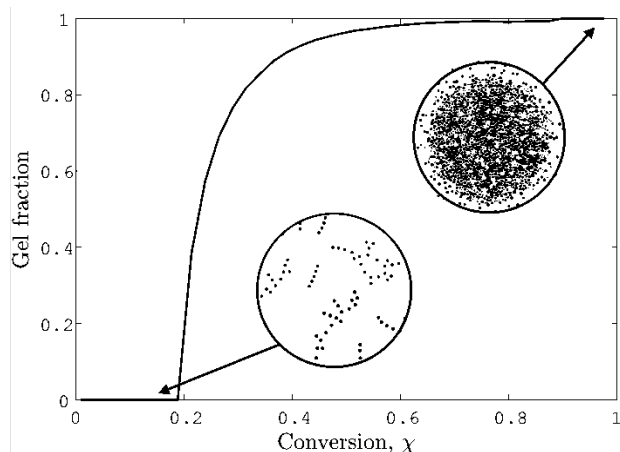


Figure 3 – Gel fraction as a function of the conversion (the degree of polymerization) with a representation of the network in the circles.

In figure 3 this process is clearly visible and in the circles representations of the network at different values of conversion are shown. At first glance, the network at full conversion looks unrealistically dense. We came up with a method to quantify this and the network at full conversion turns out to be unphysical. Therefore, adjustments to the model had to be made and this resulted in the development of the advanced model.

### Advanced model

In the advanced model three strategies are added to describe the system more accurately. The first strategy, here referred to as preferential coupling, ensures that nodes that are close together have a higher probability of connecting to each other than to a node that is far away. The second strategy is to allow intramolecular bonds to be formed. Thirdly, shielding or steric hindrance is taken into account.

#### Preferential coupling

To add the preferential coupling to the model, the absence of spatial dimensions had to be circumvented. Therefore, the preferential coupling between two nodes is based on having a common neighbor. If only one node links two nodes, the effect is the strongest and the probability of these two nodes to connect is spiked.

$$r'_{i,j} = r_{i,j} \cdot \left(1 + \alpha \sum_{p=1}^{p_{max}} A_p p^{-3/2}\right)$$

Matrix  $r_{i,j}$  is modified by multiplying it with a factor that includes matrix  $A_p$ , obtained from adjacency matrix  $A$ , that shows all nodes reachable in  $p$  steps. Matrix  $A_p$  is multiplied with path length  $p$  with a certain exponent that ensures that the effect decreases when the path between the two nodes becomes longer.<sup>11</sup> Parameter  $\alpha$  tunes the strength of the effect.

As illustrated in Figure 4, the density of the network is sensitive to the strength of preferential coupling,  $\alpha$ . In fact low values of  $\alpha$  may trigger the network to have higher than critical density. These cases can be eliminated considering a simple geometrical argument. From the volumetric perspective, the optimal shape to pack nodes is a sphere. When the volume of a sphere is doubled, the

radius does not double, but scales with a factor of  $\sqrt[3]{2}$ . Figure 4 shows the scaling factor on the y-axis for networks with different values of  $\alpha$ . For low values of  $\alpha$  the scaling factor is below the lower bound of  $\sqrt[3]{2}$ , which means that these networks are too dense.

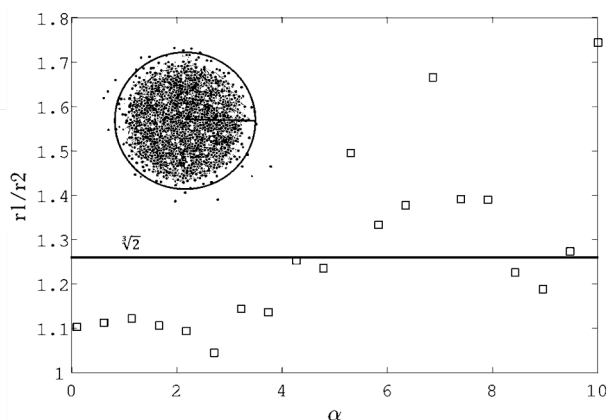


Figure 4 – Scaling factors of networks with different values of  $\alpha$ . The line is the scaling factor of the optimal shape, a sphere, and is the lower bound.

From this plot we can extract a range of values of  $\alpha$  that corresponds to networks that are not too dense and therefore physical. Preferential coupling results in a sparser network, because the nodes have the tendency to form clusters. In this case, monomers from a particular cluster are strongly connected to other monomers in the cluster, but loosely connected to the rest of the network. This is visible in figure 5, which shows two networks at full conversion, one obtained from the standard model and one with preferential coupling. As we know from figure 4, the network on the left is too dense.

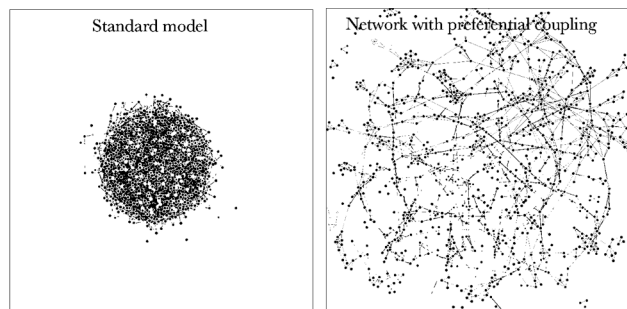


Figure 5 – Left: a network of 1000 nodes obtained from the standard model. Right: a network of 1000 nodes with preferential coupling.

### Intramolecular bonding

In the advanced model intramolecular bonds are allowed to form. These are bonds between fatty acids within one TAG-unit. This is implemented in the model by looking at the functionality of the individual fatty acids, instead of the TAG-unit as a whole. This effect is tuned by parameter  $\beta$ :

$$r_{i,j} = \begin{cases} d_i^{free} \cdot d_j^{free}, & i \neq j \\ \beta \binom{d_i^{fa}}{2}, & i = j \end{cases}$$

The intramolecular bonds postpone the gel point, because functionalities are consumed internally and the TAG-units can make fewer bonds. Therefore the network becomes less interconnected.

### Shielding

The shielding or steric hindrance of a node depends on the number of neighbors and on their shielding, which again depends on the number of their neighbors and their shielding. Subsequently, the shielding of a node depends on its own shielding. This is called an eigenvalue problem and is similar to the page ranking method Google® uses.<sup>12</sup>

### VALIDATION OF THE MODEL

In order to use the results of the model, validation of the model is necessary. An experiment is designed within our group and will be executed in the near future. It involves the hydrolysis of the TAG-units of polymerized oil paint and the result is a size distribution of the obtained fragments. The idea behind this experiment is that the gel point is postponed. The aforementioned problem with the analysis of a polymerized network is the density and complexity of the network. Basically, structural information can only be obtained before the gel point. By hydrolyzing the gel, the network is brought back to sol and therefore to the measurable regime. In the experiment, the cross-links are retained, because they are not hydrolyzed. This means that gel can still exist, although at higher values of conversion. The results can be compared to size distribution of simulated networks with different values of  $\alpha$  and  $\beta$ . In the end, the parameter set that corresponds to a real oil paint network the best can be found.<sup>13</sup> Figure 6 shows two size distributions of a hydrolyzed network for two different values of  $\beta$  (intramolecular bonding).

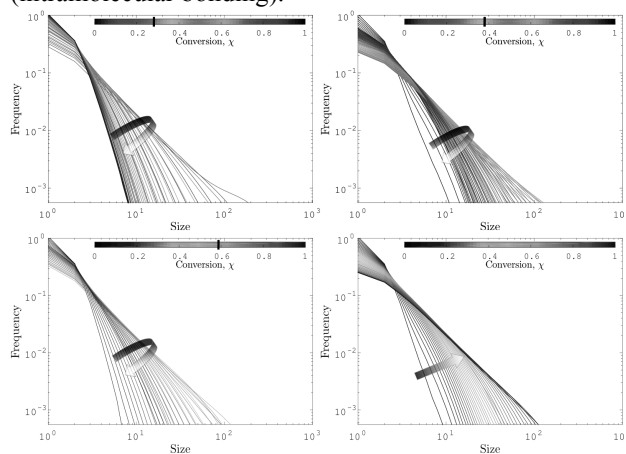


Figure 6 – Upper left: non-hydrolyzed network for  $\beta = 0.001 \cdot N$ . Upper right: hydrolyzed network for  $\beta = 0.001 \cdot N$ . Lower left: non-hydrolyzed network for  $\beta = 4 \cdot N$ . Lower right: hydrolyzed network for  $\beta = 4 \cdot N$ .

In these plots the sizes of the molecules in sol are shown on a logarithmic x-axis. In the non-hydrolyzed network for low  $\beta$  the sizes increase with conversion, until the gel point (indicated by the black line in the conversion bar) and after that the sizes decrease. This indicates that gel is formed and this gel is consuming all the loose molecules. The hydrolyzed network shows the same trend, but the gel point is postponed. The non-hydrolyzed network for high  $\beta$  still experiences gel point, although postponed by

the influence of the intramolecular bonding. A change in the trend is visible in the hydrolyzed network for high  $\beta$ ; the sizes of the molecules keep increasing. That means that no gel is formed anymore. The intramolecular bonds modify the connectivity of the network in such a way that it becomes less connected and hydrolysis of the TAG-units can completely break up the network.

### CONCLUSION

This model incorporates novel advanced routines to simulate the binding medium in oil paints that is essentially a polymer network. In the advanced model, the system is completely represented by the topology and it is also the topology that defines the reactivity of the monomers, instead of only the functionality. Because the system is represented by just a topology, there are no spatial dimensions. This makes the model time and space scalable. Space scalability means that the model is applicable to other systems. The size of the monomers of other systems is not of importance, because they can still be represented as nodes. Time scalable means that paint alterations can be studied with our model either in microseconds or in centuries.

Several examples of the influence of  $\alpha$  and  $\beta$  (parameters of the model corresponding to preferential coupling and intermolecular bonding) on the properties of the network are shown. These properties are straightforward, such as the density and gel point and more complex ones, such as the elasticity, strength and inhomogeneity. For the validation of the model, the response to hydrolysis is the most important property that is influenced by the parameters. The results of the experiment, which we plan to perform in our future work, have to be compared to results from the model. By changing  $\alpha$  and  $\beta$  the response to hydrolysis can be tuned in such a way that the simulated results approach the experimental results closely and the optimal parameter set can be found. With this parameter set the original network can be reconstructed through the model. Now, all the desired structural information about the molecular topology of the network can be extracted from the model.

Conservation science has come a long way since Van Eyck made his first oil painting and our model provides an important step towards understanding the physical properties of oil paint. These insights will help to explain the interaction of pigments with the network and the degradation processes in oil paintings; highly valuable knowledge for conservation scientists. However, the largest beneficiaries of this model may be polymer industries such as manufacturers of certain plastics and rubber, the most well known mass-produced cross-linked polymers. The experimental characterization of these polymers is limited and in this respect they are no different from oil paint. Our model can contribute to the elucidation of their molecular structure and physical properties and help improve their production process.

### ROLE OF THE STUDENT

Jorien Duivenvoorden was the undergraduate student under the daily supervision of dr. I. Kryven. Supervisors dr. I. Kryven and prof. dr. P.D. Iedema designed the research. The student developed the numerical code of the

model together with dr. I. Kryven. Additionally, the student performed extensive numerical simulations on supercomputer Lisa. Furthermore, the student analyzed the data, gave a presentation on the results and finally wrote a thesis and this summary about the research.

### REFERENCES

1. Van den Berg, J., Van den Berg, K., Boon, J. Determination of the degree of hydrolysis of oil paint samples using a two-step derivatisation method and on-column GC/MS. *Progress in Organic Coatings*, 41 (2001), 143-155.
2. Geldof, M. Finding the suspect of the discolouration of the floor. <http://slaapkamergeheimen.vangoghmuseum.nl/category/collaboration/?lang=en>
3. Hamzehlou, S., Reyes, Y., Leiza, J.R. A new insight into the formation of polymer networks: a kinetic monte carlo simulation of the cross-linking polymerization of s/dvb. *Macromolecules*, 46 (2013), 9064-9073
4. Soucek, M. D., Khattab, T., Wu, J. Review of autoxidation and driers. *Progress in Organic Coatings*, 73 (2012), 435-454.
5. Van Gorkum, R., Bouwman, E. The oxidative drying of alkyd paint catalysed by metal complexes. *Coordination Chemistry Reviews*, 249 (2005), 1709-1728.
6. Mastan, E., Zhu, S. Method of moments: A versatile tool for deterministic modeling of polymerization kinetics. *European Polymer Journal*, 68 (2015), 139-160.
7. Kryven, I., Iedema, P. D. Transition into the gel regime for free radical crosslinking polymerisation in a batch reactor. *Polymer*, 55 (2014), 3475-3489.
8. Kryven, I., Iedema, P. D. Topology evolution in polymer modification. *Macromolecular Theory and Simulations*, 23 (2014), 7-14.
9. Rapaport, D. C. *The art of molecular dynamics simulation*. Cambridge University Press, Cambridge, UK, 2004.
10. Gillespie, D.T. A general method for numerically simulating the stochastic time evolution of coupled chemical reactions. *Journal of computational physics*, 22 (1976), 403-434
11. Dušek, K.; Gordon, M.; Ross-Murphy, S.B. Graphlike state of matter 10. Cyclization and concentration of elastically active network chains in polymer networks. *Macromolecules*, 11 (1978), 236-245.
12. White, B. Math 51 lecture notes: How Google ranks web pages. <http://web.stanford.edu/class/math51/PageRank.pdf>
13. Chakraborty, J., Kumar, J., Singh, M., Mahoney, A. W., Ramkrishna, D. Inverse Problems in Population Balances. Determination of Aggregation Kernel by Weighted Residuals. *Industrial & Engineering Chemistry Research* (2015)