

# Simplified Closed Form Numerical Approaches to Predict Natural Rubber Behavior under Sulfur Curing in Standard Rheometer Tests

Marco Brotto<sup>1</sup>, Gabriele Milani<sup>2</sup> and Federico Milani<sup>1</sup>

<sup>1</sup> CHEM.CO Consultant, Via J.F.Kennedy 2, 45030 Occhiobello (RO), Italy

<sup>2</sup> Technical University in Milan, Piazza Leonardo da Vinci 32, 20133 Milan, Italy

**Keywords:** Rubber Vulcanization, NR, Numerical Model, Kinetic Approach.

**Abstract:** In this paper, a complex numerical and a simplified mathematical closed form approach with robust kinetic base are proposed to interpret NR sulfur vulcanization. A preliminary phase of preparation of meta-rheometer curves from few experimental data may be necessary to have at disposal the whole curve to fit with the model when experimental data at disposal are a few. Then, on such data (either experimental or artificially generated) partial reaction kinetic constants characterizing the vulcanization process within the models proposed are derived. When needed, meta-data are obtained using a direct C2 natural cubic spline interpolation of the rheometer curve, which proved to fit the experimental data well. Both the presence and absence of reversion are discussed and how they are reflected in the model calculations. The chemical schemes, translated mathematically into differential equations systems, are suitably re-arranged to derive single analytical equations, which represents the crosslinking degree evolution vs time. The parameters of the single equations may be determined setting the kinetic constants of the chemical model by means of best fitting in the first model (more complex) and with the direct solution of a non linear system of equations in the second (simplified) approach. The major improvement of the second procedure here proposed is to utilize some ad hoc values for the kinetic constants that do not necessarily require an optimization algorithm, thus by-passing the usage of a least squares minimization routine.

## 1 INTRODUCTION

Sulphur vulcanization maybe represents the most popular technique to cure both natural rubber (NR) and its synthetic counterpart (IR), as well as for other synthetic rubbers such as polybutadiene (BR), styrene-butadiene rubber (SBR), nitrile rubber (NBR), butyl rubber (IIR), and ethylene-propylene-diene rubber (EPDM), only to indicate the most important in the market. In general, it is commonly accepted that vulcanization takes place roughly into three steps: induction, crosslinking and post crosslinking. The idea comes from the macroscopic interpretation of what happens to a sample during controlled temperature curing conditions in the rheometer chamber. The rheometer curve, which is simply the measure of the torque resistance of a sample subjected to fixed temperature cure at increasing time, typically exhibits an initial plateau with low and slightly decreasing torque, a rapid crosslinks formation with a significant torque increase and eventually a final degradation, i.e. a

torque decrease, at sufficiently large vulcanization times, usually denoted with the term “reversion”. Reversion is a key distinctive aspect of the vulcanization with sulphur and, from a macroscopic point of view, consists in a remarkable decrease or rubber vulcanized properties at the end of the curing process. It depends on a series of concurring factors, the most important being rubber type, its structure, % of double bonds see (Milani and Milani, 2012), presence of additives, in particular the accelerators, and co-adjuvants, as well as vulcanization temperature.

In the paper, two numerical models to interpret natural rubber vulcanization with reversion are presented: a complex and a simplified one. Both of them have robust kinetic base. A preliminary phase of preparation of meta-rheometer curves from few experimental data may be necessary to have at disposal the whole curve to fit with the model when experimental data at disposal are a few. In this latter case, meta-data are obtained using a direct C2 natural cubic spline interpolation of the rheometer

curve, which proved to fit the experimental data reasonably well. On either experimental or artificially generated data, two kinetic schemes are assumed to fit rheometer curves, the first involving 5 kinetic constants, the second only 2. The chemical schemes, translated mathematically into differential equations systems, are suitably re-arranged to derive single analytical equations, which represents the crosslinking degree evolution vs time. Kinetic constants of the first model are derived by means of a best fitting procedure, whereas in the second model the solution of a two variables non linear system of equations is needed. The major improvement of the second procedure here proposed is avoid the utilization of an optimization algorithm, which sometimes proved to be not sufficiently robust. Both models are validated on a wide set of experimental data available in the literature.

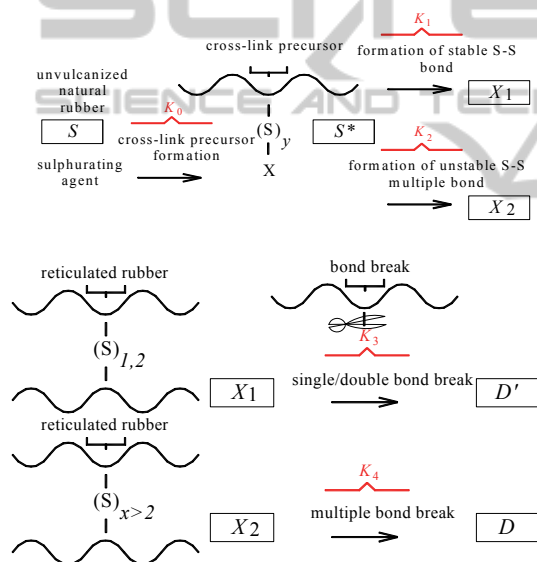


Figure 1: Products and schematic reaction mechanisms of NR accelerated sulphur vulcanization.

## 2 META-DATA GENERATION WITH NATURAL CUBIC SPLINES

When a few “characteristic” experimental points on the rheometer curve are available, i.e. when the entire cure curve is not at disposal, a natural cubic spline interpolation of the experimental data at hand, which typically include a few “meaningful” points may be used to produce a meta-curve approximating the experimental rheometer one, see (Milani and

Milani, 2014a; Milani and Milani, 2014b). Instead of MHF the reversion percentage, i.e. the decrease in the peak torque at the end of the rheometer test, may be provided.

The fundamental idea behind cubic spline interpolation is based on the engineer’s tool used to draw smooth curves through a number of points of the actual rheometer curve  $M(t)$ .

Spline interpolation is based on the following hypotheses:

- 1) The piecewise function  $M(t)$  interpolates all data points.
- 2)  $M(t)$  together with its first and second derivatives ( $M'(t)$  and  $M''(t)$  respectively) are continuous on the interval  $0-t_{max}$ .

The kernel, Deitel relies on the fitting of known experimental points at times  $t_1, t_2, \dots, t_n$  by means of a piecewise function of the form:

$$M(t) = \begin{cases} M_1(t) & \text{if } t_1 \leq t \leq t_2 \\ M_2(t) & \text{if } t_2 \leq t \leq t_3 \\ \dots \\ M_{n-1}(t) & \text{if } t_{n-1} \leq t \leq t_n \end{cases} \quad (1)$$

where  $M_i$  are third degree polynomial defined by

$$M_i(t) = a_i(t-t_i)^3 + b_i(t-t_i)^2 + c_i(t-t_i) + d_i$$

with  $i = 1, 2, \dots, n-1$ .

The previous interpolating function has first and second derivative equal to:

$$\begin{aligned} dM_i(t)/dt &= 3a_i(t-t_i)^2 + 2b_i(t-t_i) + c_i \\ d^2M_i(t)/dt^2 &= 6a_i(t-t_i) + 2b_i \end{aligned} \quad (2)$$

Assuming that the composite function passes through experimental points (say that, at  $t_i$ , the rheometer curve has a torque equal to  $\bar{M}_i$ ), it is continuous with its first and second derivatives (equal to  $\bar{M}_i'$  and  $\bar{M}_i''$  in  $t_i$  respectively) we obtain  $2n-2$  mathematical conditions from the passage through points and  $2(n-2)$  conditions for the first and second derivative continuity respectively.

Total coefficients to set are  $4(n-1)$ , so that the number of coefficients exceed equality conditions by 2 equations.

In order to evaluate the degree of vulcanization  $\alpha_{exp}(t)$ , see (Milani et al., 2013) and (Sun et al., 2009), the following relation may be used:

$$\alpha_{\text{exp}}(t) = \frac{S'(t) - S_{\min T}}{S_{\max T_0} - S_{\min T_0}} \quad (3)$$

where:

-  $M_{\min T}$  is the minimum value of torque  $M(t)$  during a cure experiment at temperature  $T$ . Before reaching this minimum value,  $\alpha_{\text{exp}}(t)$  is considered equal to zero.

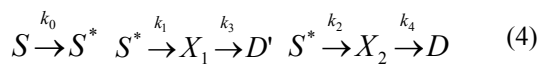
-  $M_{\min T_0}$  and  $M_{\max T_0}$  are the minimum and maximum torque values obtained for a cure experiment at a temperature  $T_0$  low enough to allow reversion to be neglected.

In this way, the rheometer curves to fit always range between 0 and 1, with a maximum torque sensibly less than 1 for high vulcanization temperatures.

### 3 A REFINED FIVE CONSTANTS KINETIC MODEL

A mechanistic model, already presented in (Milani et al., 2013), based on a detailed kinetic scheme, is here recalled. The mathematical solution of the mechanistic model allows to numerically reproduce rheometer curves for NR vulcanized with sulfur. The basic reaction schemes are schematically represented in Figure 1. Such scheme simplifies well established chemical interpretations available from the technical literature, see (Ding and Leonov, 1996; Han et al., 1998; Leroy et al., 2013).

Adopting for NR the kinetic scheme constituted by the chemical reactions shown in Figure 1, the following schematization holds:



In Equation (4),  $S$  is the uncured polymer,  $S^*$  the unmatred crosslinked polymer, which evolves into matured crosslinked polymer  $X_1 + X_2$ , with  $X_1$  indicating the stable crosslinked part and with  $X_2$  the unstable part. Part of both  $X_1$  and  $X_2$  may evolve into  $D$  and  $D'$  unvulcanized polymer due to multiple S-S chains breaks and consequent backbiting.  $K_{0,\dots,4}$  are kinetic reaction constants.

Here it is worth emphasizing that  $K_{0,\dots,4}$  are temperature dependent quantities, hence they rigorously should be indicated as  $K_{0,\dots,4}(T)$ , where  $T$  is the absolute temperature. In what follows, for

the sake of simplicity, the temperature dependence will be left out.

Differential equations associated to chemical reactions are the following:

$$\begin{aligned} \text{(a)} \quad & \frac{dS}{dt} = -K_0 S \\ \text{(b)} \quad & \frac{dS^*}{dt} = K_0 S - (K_1 + K_2) S^* \\ \text{(c)} \quad & \frac{dX_1}{dt} = K_1 S^* - K_3 X_1 \\ \text{(d)} \quad & \frac{dX_2}{dt} = K_2 S^* - K_4 X_2 \end{aligned} \quad (5)$$

A closed form solution for the crosslink degree, intended as  $\alpha = X_1 + X_2$ , may therefore be deduced from relations (7). In particular, the variation of the cure degree as a function of time  $t$  assumes the following form:

$$\begin{aligned} \alpha = X_1 + X_2 = & C_4 e^{-K_4 t} + C_6 e^{-K_3 t} + \\ & - C_2 \frac{K_1}{K_1 + K_2 - K_4} e^{-(K_1 + K_2)t} + \\ & - C_2 \frac{K_2}{K_1 + K_2 - K_3} e^{-(K_1 + K_2)t} + \\ & - \frac{K_0 K_1 S_0}{(K_1 + K_2 - K_0)(K_0 - K_4)} e^{-K_0 t} + \\ & - \frac{K_0 K_2 S_0}{(K_1 + K_2 - K_0)(K_0 - K_3)} e^{-K_0 t} \end{aligned} \quad (6)$$

Having indicated with  $C_2$ ,  $C_4$  and  $C_6$  the following integration constants:

$$\begin{aligned} C_2 = & - \frac{K_0 S_0}{K_1 - K_0 + K_2} \\ C_4 = & \frac{K_0 K_1 S_0}{(K_0 - K_4)(K_1 + K_2 - K_4)} \\ C_6 = & \frac{K_0 K_2 S_0}{(K_0 - K_3)(K_1 + K_2 - K_3)} \end{aligned} \quad (7)$$

and with  $S_0$  the initial amount of unvulcanized polymer, which, as already mentioned, has to be put equal to 1 when the crosslink percentage  $\alpha$  (ranging from 0% to 100%) has to be determined.

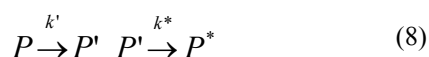
### 3.1 Starting Point Determination

In order to evaluate kinetic constants of the model (problem (4)), a non-linear least squares routine -to fit with the mathematical model normalized rheometer curves- has to be used, see (Milani et al., 2013). The utilization of non-linear optimization algorithms is not always effective, may fail in some cases in finding the minimum point or may require an excessive processing time. Two alternative strategies are possible, the first is to find a reasonable starting point, intending with the term reasonable a point sufficiently near the solution of the least-squares problem. Such procedure is however not an easy task in this case and the starting point determination is usually done by attempts, discriminating the quality of the starting point looking at the stability of the algorithm. An alternative is to simplify the kinetic scheme and compare the results obtained with those provided by the mathematical solution of problem (4).

## 4 THE NEW SIMPLIFIED MECHANISTIC MODEL PROPOSED

In this section, we propose a novel, simplified but robust mechanistic model to fit experimental rheometer curves that do not require the least squares data fitting, mandatory for solving problem (4).

According to the chemical reactions reported in Figure 1, it is possible to analyze the problem by means of the following simplified kinetic model:



Where  $K' = K_1 + K_2$  and  $K^* = K_3 + K_4$ .

Differential equations associated to chemical reactions are the following:

$$\begin{aligned} (a) \quad & \frac{dP}{dt} = -K' P \\ (b) \quad & \frac{dP'}{dt} = K' P - K^* P' \\ (c) \quad & \frac{dP^*}{dt} = K^* P' \end{aligned} \quad (9)$$

Differential Eq. (9)(a) may be solved immediately providing  $P(t)$  as  $P(t) = P_0 e^{-K't}$ . The previous equation may be substituted into Eq. (9) (b) providing directly a differential equation for  $P'(t)$ , which represents the matured polymer as:

$$\frac{dP'}{dt} + K^* P' = P_0 K' e^{-K't} \quad (10)$$

which is solved in closed form finding a general integral and a particular solution.

The general integral is the following:

$$P'_g = C_1 e^{-K^*t} \quad (11)$$

whereas a particular integral is:

$$P'_p = C_1 e^{-K^*t} - P_0 \frac{e^{-K't} e^{-(K'-K^*)t}}{K'-K^*} \quad (12)$$

So that the solution of the differential equation under study is:

$$P' = C_1 e^{-K^*t} - P_0 \frac{e^{-K't} e^{-(K'-K^*)t}}{K'-K^*} \quad (13)$$

Assuming that  $P'(0) = 0$ , hence Eq. (13) becomes:

$$P'(t) = \frac{P_0}{K'-K^*} e^{-K^*t} \left( 1 - e^{-(K'-K^*)t} \right) \quad (14)$$

Assuming that at  $t_1$  the rheometer curve reaches a maximum and that at  $t_2$  the reversion percentage is, say,  $R$ , it is possible to directly evaluate  $K'$  and  $K^*$  by means of the solution of a non linear system of equations (two equations in two variables).

## 5 MODEL VALIDATION

A full validation of the approach proposed has been already performed on the 5 kinetic constant model, considering some experimental data available in the technical literature, see (Davis et al., 1986), where a NR blend is vulcanized with sulphur, in presence of different accelerators at the same curing temperature (144°C). The accelerators proved, in some cases, to give the blend an excellent reversion resistance.

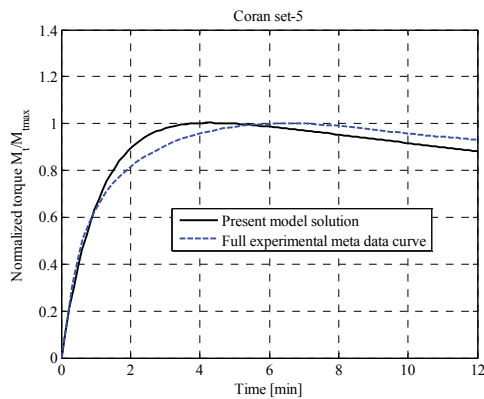


Figure 2: preliminary simplified model validation on data set 5 of Table 1 and Table 2.

The performance of the accelerators was comparatively estimated collecting a few rheometer data, as for instance  $t_2$  and  $t_{90}$  times, reversion %, total cure time, maximum torque and some mechanical properties of the cured specimens, as elongation at break, ultimate tensile strength and elastic modulus at 300% of elongation. Information regarding the behaviour of the blend in the rheometer chamber is particularly suitable to calibrate meta data in the first step.

A preliminary validation of the simplified procedure proposed in this paper is still running and is under study by the authors. However, first results obtained on some data sets, see e.g. Figure 2, seem to confirm a generally satisfactory capability of the numerical model to fit reasonably well the main features of the experimental rheometer curves, i.e. amount of reversion and time needed to achieve an optimal vulcanization.

When dealing with specific chemical aspects of the validation, it is possible to compare synoptically the numerical results obtained in terms of kinetic constants (5 constants model), see Figure 3, with reference to the experimental results available, see Table 1 and Table 2.

Using dialkyldithiophosphates (as ZDBDP) it is possible to obtain improved reversion resistance, see (Davis et al., 1986). However, blends containing such accelerators generally burn slightly on the surface and this affects their practical use. ZDBDP with TBBS is a accelerators combination that decreases drastically the cure time needed, but with a very short scorch delay. With about a stoichiometric equivalent by w. of CTP, roughly the same improvements in the curing rate with very small reversion may be obtained. Finally, certain triazine derivatives have been identified as active

accelerators however, increasing their amount in the blend also with the PSSR accelerator resulted into superficial burn.

Table 1: Overview of the experimental data utilized to validate the two-step numerical model (1/2).

Numerical Test #	1	10	5	6	11	9
Reversion %	19.1	17.1	12.1	9.5	6.5	3.9
M300 [MPa]	15.2	11.8	14.5	14.3	15.0	18.5
UST [MPa]	28.8	27.5	28	27.1	26.0	29.0
UE [%]	517	574	499	510	477	459
Cure time [min]	25	21.2	36.5	30.0	50.7	29
ODR 144°C						
$t_2$ [min]	9.2	4.65	10.5	9.5	10.9	10.5
$t_{90}$ [min]	21.6	17.4	31.7	25.5	45.8	25.2
Products concentration in phr						
PYSSPY					1.0	1.0
MBS						0.25
TBBS	0.6					
TSSR			0.7	1.0		
MBTS		1.0				

Table 2: Overview of the experimental data utilized to validate the two-step numerical model (2/2).

Numerical Test #	4	8	7	2	3
Reversion %	6.1	9.0	5.7	5.6	6.5
M300 [MPa]	15.5	11.6	16.8	13.0	13.2
UST [MPa]	28.0	25.0	27.1	28.0	28.0
UE [%]	503	544	464	555	550
Cure time [min]	29	43	26	13	24
ODR 144°C					
$t_2$ [min]	7.8	15.3	9.5	5.7	14.7
$t_{90}$ [min]	25	37.6	22.5	12.0	22.0
Products concentration in phr					
TSST	0.7				
PSSR		1.0	0.5		
TSSR			0.5		
TBBS				0.2	0.2
ZDBDP				0.76	0.76
CTP					0.72

Finally, plotting the numerical constants found with the 5 kinetic constants model as in Figure 4 (in subfigure –a a relationship between  $K_3+K_4$  and reversion % is provided whereas in subfigure –b a relationship between  $K_1+K_2$  and cure time is shown) it is very straightforward to conclude that  $K_3+K_4$  (which follow almost rigorously a straight line for the reversion) globally gives a quantitative information on the amount of degradation of cure, whereas  $K_1+K_2$  the speed of reticulation. Best fitting curves reported in Figure 4 may be therefore

extremely useful from a practical point of view to directly predict the most important parameters of vulcanization of a rubber blend, i.e. time needed for curing and expected reversion.

## 6 CONCLUSIONS

Two kinetic models suitable -to interpret NR vulcanization in presence of reversion- through the utilization of the experimental rheometer curve have been presented. Depending on the level of complexity of the kinetic model proposed, more detailed or less precise information on the degree of curing, as well as on the single and multiple-bond percentage of resulting links may be retrieved. However, an increased complexity of the models results both into the impossibility to deal with closed-form predicting expressions for the cure percentage and in complex numerical best fits on experimental data available to estimate single kinetic constants representing the chemical scheme adopted.

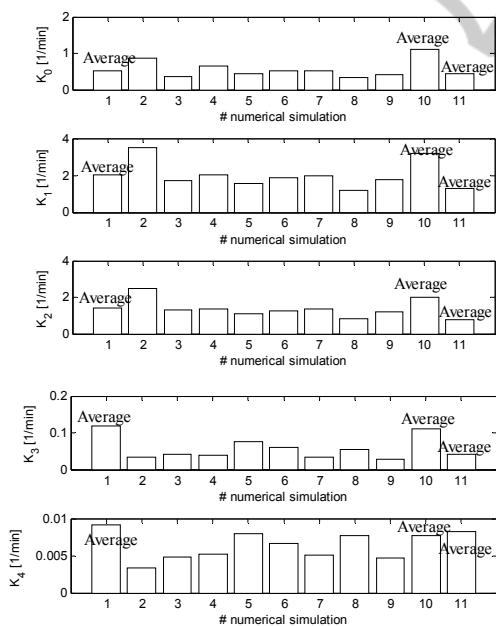


Figure 3: Synoptic comparison between the partial kinetic constants obtained in the different cases analyzed numerically.

Two models of different complexity have been presented: the first describes in a quite complex way the vulcanization process and requires the knowledge of five kinetic constants, the second is rougher but less complex, needing only the evaluation of two kinetic constants.

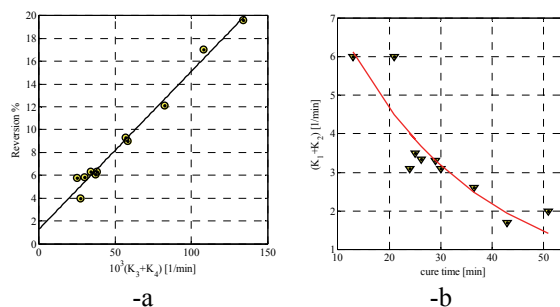


Figure 4: -a: Relationship between  $K_3+K_4$  and reversion %. -b: relationship between  $K_1+K_2$  and cure time.

The first approach proved to fit very well experimental rheometer curves (or meta-curves deduced numerically from few experimental data available), but needs expensive and not always robust best fitting procedures, whereas the second is less precise but allows the determination of model constants directly by mean of the solution of a non-linear equations system into only two variables.

The validation of the simplified model is still running. In particular, the choice of the two points into the rheometer curve to select in order to obtain the best performance of the model (in terms of fitting) appears the key issue to be investigated.

## REFERENCES

- ASTM D 2084-81, Annual Book, 1986.
- Davis, L.H., Sullivan, A.B., Coran, A.Y., 1986. New curing system components. In Proc.: International Rubber Conference IRC 86 – Goeteborg, Sweden , vol.2 , p.387-392.
- Ding, R., Leonov, I., 1986. A kinetic model for sulfur accelerated vulcanization of a natural rubber compound. *J. Appl. Polym. Sci.*, 61, 455.
- Han, I.S., Chung, C.B., Kang, S.J., Kim, S.J., Chung, H.C., 1998. A kinetic model of reversion type cure for rubber compounds. *Polymer (Korea)*, 22, 223.
- Leroy, E., Souid, A., Deterre, R., 2013. A continuous kinetic model of rubber vulcanization predicting induction and reversion. *Polym. Test.*, 32 (3), 575.
- Milani, G., Milani, F., 2010. A new simple numerical model based on experimental scorch curve data fitting for the interpretation of sulphur vulcanization. *J. Math. Chem.*, 48, 530.
- Milani, G., Milani, F., 2012. Comprehensive numerical model for the interpretation of cross-linking with peroxides and sulfur: Chemical mechanisms and optimal vulcanization of real items. *Rubber Chem. Technol.*, 85 (4), 590.
- Milani, G., Leroy, E., Milani, F., Deterre, R., 2013. Mechanistic modeling of reversion phenomenon in

- sulphur cured natural rubber vulcanization kinetics. *Polym. Test.*, 32, 1052.
- Milani, G., Milani F., 2014a. Fast and reliable meta-data model for the mechanistic analysis of NR vulcanized with sulphur. *Polymer Testing*, 33(1), 1.
- Milani, G., Milani F., 2014b. Effective closed form starting point determination for kinetic model interpreting NR vulcanized with sulphur. *Journal of Mathematical Chemistry*, 52(2), 464.
- Sun, X., Isayev, A., 2009. Cure kinetics study of unfilled and carbon black filled synthetic isoprene rubber. *Rubber Chem. Technol.*, 82(2), 149.
- Westlinning, H., 1970. Vulcanization of Rubber with Aminomercaptotriazines. *Rubber Chem. Tech.*, 43, 1194.

